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In this issue :

	PAGE
Title Pages, Contents, and List of Plates	i
Minutes of Proceedings :	
Annual General Meeting, London, 1949	xvii
May Lecture, London, 1949	xxxvi
Annual Autumn Meeting, Paris, 1949	xl
General Meeting, London, November 1949	li
Discussion and Correspondence on Papers Presented at the Annual Autumn Meeting, Paris, 1949	1103
Obituary Notices	1208
Name Index to the Journal, 1948-49, Volume 75, and Monographs No. 5, 7, and 8	1211

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SYMPOSIUM ON METALLURGICAL ASPECTS OF THE HOT
WORKING OF NON-FERROUS METALS AND ALLOYS.

THE HOT ROLLING OF ALUMINIUM AND ITS ALLOYS.* 1225

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(Contribution from The British Aluminium Co., Ltd.)

SYNOPSIS.

A general description is given of current practice in the hot rolling of aluminium and its alloys, together with a discussion of the various considerations leading to the adoption of the methods employed. In addition, the question of the preheating of the rolling slab is considered. The paper also contains an account of the physical and metallurgical aspects of hot rolling, including a detailed discussion of the mode of deformation. It is suggested that in the hot rolling of aluminium the metal behaves as a very viscous fluid, and that while there is no roll-face slip there is considerable relative movement of the various layers of the metal. The bearing of this upon some of the practical problems of the process is considered. The effect of hot rolling upon the metallurgical constitution of the metal is also dealt with, and some indication is given of the influence of hot-rolling variables upon the behaviour of the finished product after final cold rolling to gauge.

INTRODUCTION.

STRICTLY speaking, the term "hot rolling" should be applied only to rolling in such a temperature range that recrystallization of the metal occurs continuously throughout the rolling operation, and the metal as it comes off the mill is in the fully annealed condition. But in practice, with aluminium, "hot rolling" is continued down to thicknesses where the temperature has fallen below that at which recrystallization takes place; indeed, with some of the alloys, it is doubtful whether any recrystallization at all takes place during the so-called hot rolling. In such cases, despite the undoubted occurrence of some stress relief or recovery, the usual effects of cold work become apparent as the metal thickness is reduced, and normal mechanical testing, after the "blank" has cooled to room temperature, shows increasing proof and ultimate tensile stresses with decreasing elongation.

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In this paper the term "hot rolling" is used in a wider sense to include all rolling operations carried out on the hot mill, irrespective of whether recrystallization is taking place or not. The paper is divided into two main parts. In Part I is given a description of current practice in the hot rolling of aluminium, together with a discussion of the various considerations leading to the adoption of the methods employed. In addition, the question of the preheating of the rolling blocks is considered. Part II contains an account of the physical and metallurgical aspects of hot rolling, including a detailed discussion of the mode of deformation and its bearing upon some of the problems mentioned in Part I. The constitutional effects of the process are also discussed in Part II, and some indication is given of the influence of hot-rolling variables upon the behaviour of the finished product after final cold rolling to gauge.

I.—HOT-ROLLING PRACTICE.

SOME GENERAL CONSIDERATIONS.

Essentially, the operation of hot rolling embraces the preheating of cast slabs to a predetermined temperature, and their reduction while still hot, by a succession of passes on one or more mills, to a "blank" of suitable gauge and properties for subsequent cold rolling. The rolling from slab to blank is commonly known in the industry as "breaking down".

As they represent the intermediate stage between casting and cold rolling, however, the particular breaking-down conditions employed are subject to the alloy and cast-block characteristics on the one hand, and to the cold-rolling and finished-sheet requirements on the other. Thus, while the definition of breaking down is broad enough to be generally applicable, differences in plant and technique are to be expected between one factory and another. To mention but one of these differences; one section of the industry will complete hot rolling on one roll stand only, while another may use as many as seven. The variations in practice thus to be observed largely reflect the history of the industry's development. Particularly in recent years, the move towards larger finished sheet and plate sizes, and very much higher output rates, has been rapid. The modern factories erected in this period have therefore tended to be equipped with large, high-speed strip mills, the economic use of which demands the heaviest coils possible. The associated hot mills are therefore designed to handle much larger slabs at higher speeds than hitherto, and a general tendency to use more mill stands for the operation may be discerned.

Large slabs are an integral feature of the modern plant; and their availability is due to the development of semi-continuous casting, which, since 1939, has largely supplanted the older chill-casting method. The adoption of semi-continuous casting has had several repercussions on hot-rolling practice, since the characteristics of the cast slab differ in a number of respects from those of its chill-cast counterpart. A consideration of the salient differences is therefore relevant to any outline of hot-rolling practice.

EFFECT OF CASTING CONDITIONS.

The rapid increase in slab size, associated with the change-over to semi-continuous casting, has already been mentioned. As a measure of the increase, it may be stated that whereas a chill-cast slab $15 \times 9 \times 30$ in., weighing 400 lb., was one of the largest in common use in 1939 (even though not the largest cast), semi-continuously cast slabs up to $48 \times 8 \times 120$ in., weighing 4500 lb., are now common, and larger sizes are projected.

Given suitable degassing and pouring techniques, a slab free from porosity is more readily obtained by semi-continuous than by chill casting. An important feature of porosity is that it may give rise to a central plane of weakness along which failure may occur during hot rolling. Some aluminium alloys, such as those with $3\frac{1}{2}\%$ and 5% magnesium and also D.T.D. 390 and 687, are more prone than others to this kind of failure. The fracture, when it occurs, does so in a plane parallel to the major faces, and the two halves open out like a crocodile's jaws; the defects are therefore termed "crocodiles". It is an observed fact that heavy drafts minimize the incidence of the trouble; but where drafts are necessarily light through power or other limitations, the presence or absence of porosity may be the determining factor in respect of crocodiling.

The macrostructure of a slab cast by the semi-continuous process differs from that of a chill-cast slab. In some cases, a finer grain, with beneficial effects on workability, is obtained; in others, such as 99.7 and 99.8% purity aluminium, crystal size may be so large that special control is required if cracking during hot rolling is to be avoided. These macrostructural characteristics of the slabs have an influence upon the directional properties of the finished strip.

The semi-continuously cast slab is cooled far more rapidly than the chill-cast slab, and as one result, high internal stresses are engendered. These may be of no consequence in the softer metals, but in higher-strength alloys, such as D.T.D. 390 and 687, they may cause serious rejections for cracking at the casting stage. Since the stresses are

materially influenced by the slab dimensions, the latter may have to be chosen to keep rejections low. The most suitable casting dimensions may not be the optimum for rolling, and, further, the variety of sizes fed to the mill increases the difficulty of running it at maximum efficiency. More careful control of initial preheating rate may also be necessary if high internal stresses are not to be momentarily increased to the point of causing cracks.

The very high chilling rate in semi-continuous casting has an additional consequence in the slabs being further removed from constitutional equilibrium than are the chill castings. Eutectics absent from the latter, may therefore be present in the former, and by their presence demand more precise control of preheating conditions if overheating, and cracking during rolling, are to be avoided. The temperature limitation may restrict the drafts applicable, so that where conditions are critical, crocodiling and curling may be encountered. The composition gradients in these slabs may also lead—notably in the case of $1\frac{1}{4}\%$ manganese alloy—to recrystallization characteristics such that the grain-size in the finished sheet is unacceptably coarse, unless the heating rate in annealing is extremely rapid. Where these conditions obtain, it is common practice to aim at constitutional equilibrium before hot rolling, by “homogenizing” the block. Since homogenization treatments involve long periods at high temperatures (e.g. 12–30 hr. at $570^{\circ}\text{C}.$) the increased demands on preheating capacity made by semi-continuous casting, are accentuated.

THE PREHEATING FURNACE.

Hot-Rolling Temperatures.

Normally, the aim is to roll at the highest possible temperature, so that the metal may be as soft as possible for rolling. Beneficial effects on the grain-size and directionality in the finished sheet are added reasons for the maximum temperatures. Clearly, however, an upper limit is set by the presence of eutectics, and by hot shortness in rolling; and the practical working limit has to take account, not only of the gradients between the point of measurement and other parts of the slab, but also, in the case of the semi-continuous casting, of an un-machined edge of the slab fairly rich in inverse segregate. To exceed the predetermined working limit is to encounter excessive cracking on the slab faces and edges during breaking down.

The lower limit of the temperature range is set by several considerations. Firstly, and most obviously, if temperature is too low, the slab may be too hard for the desired overall reduction to be effected, or for

the application of the individual heavy drafts which minimize the chances of crocodiling and edge cracking, and help to produce a fine grain-size in the finished sheet. Secondly, since the response of cold-rolled metal to annealing is influenced by the hot-rolling temperature, too wide a range is undesirable. Thirdly, the hot-rolling temperature may influence the type and degree of preferred orientation in the finished sheet; and since the change can be quite sharp as rolling temperatures vary round 500°C ., the permissible rolling range may be narrowed on this account also. These restrictions on the temperature range apply from one part of a slab to another, as well as from slab to slab.

The result of these conditions is to enforce quite narrow working ranges, and with them the necessity for precise control of the preheating furnaces.

Features of Typical Furnaces.

The modern preheating furnace has therefore an exacting duty to perform. It must handle large slabs, and yield high outputs; outputs and temperature control must be maintained despite the charging of a variety of slab sizes, and the necessity for relatively high temperatures, and, in some cases, for long times at those temperatures.

The high outputs required may be obtained by using either a large number of small furnaces or a smaller number of large furnaces; the former arrangement has the advantage of flexibility where a large number of alloy programmes requiring different rolling temperatures has to be met. The general tendency is to adopt the larger units with outputs in the region of 5–10 tons/hr., and there is increasing pressure on the furnace designer to improve outputs still further without sacrifice of close temperature control. The furnaces may be designed for either batch or continuous operation.

Town-gas, producer-gas, oil, and electric-resistor heating are all successfully used, and it is customary to "zone" the furnace chamber for temperature-control purposes, each zone being under separate thermostatic control. Since the machined aluminium slabs are good heat reflectors, heat transfer by radiation is relatively inefficient, and in general conduction and convection are relied upon, there being a general tendency for gas velocities to be increased as a result of the continued demands for increased outputs, higher temperatures, and closer temperature control. To achieve this control very careful attention must be given to the velocity and direction of the gas circulation, and reversing regenerative flow may, in modern units, replace the more common unidirectional flow.

Where gas and oil fuels are used, greater attention is being paid to

the avoidance of condensation on the surfaces of slabs entering the furnace, since this may cause objectionable staining, and impair adhesion of the cladding in clad alloys.

It is usual to work with a slight positive pressure in the furnace chamber, to avoid the ingress of cold air which would accompany the frequent opening of doors.

THE HOT ROLLING MILLS.

The complete breaking-down operation involves a reduction in thickness from the 8-10 in. of the cast slab to the 0.200 in., or even 0.100 in., of the blank for cold rolling. Ability to achieve this in the minimum number of passes is clearly an economic advantage. But heavy drafts also have technical advantages in reducing crocodiling, edge cracking, and grain-size, as mentioned earlier in the paper, and by virtue of the shorter rolling time give a hotter blank at the later passes, so that flatness is more readily controlled. Heavy drafts are always the aim in hot rolling therefore; and the maximum that can be taken depends upon the horse-power available, the width, thickness, and properties at temperature of the alloy being rolled, the roll diameter, and the coefficient of friction between stock and roll. In particular, horse-power available, roll diameter, and coefficient of friction must be high.

The reduction from the 8-10 in. of the slab to the final blank thickness may be done in a number of different ways. The simplest way, and one which is still largely used, is to employ a single two-high reversing mill for the whole of the hot rolling.

Another practice favours the transfer of the partly rolled slab at between 3 and 5 in. thickness to a four-high reversing stand; this transfer may be with or without a second heating of the slab.

Finally, this four-high reversing mill may itself either complete the hot-rolling process or else the partly rolled blank may be transferred at a thickness of $\frac{1}{2}$ – $\frac{3}{4}$ in. to a continuous train of from two to five four-high, non-reversing stands, where it may be rolled to a final thickness of 0.1-0.125 in.

There are thus many possible variants, from the single two-high reversing mill of the older plants to the complete train of rolls found in the more modern American equipments. One of the intermediate possibilities, recently described by Matter and Lamourediedieu,¹ is that used at the Issoire Plant of the Société Centrale des Alliages Légers. Here the first mill is a four-high reversing mill, and the first two stages are combined, the slab being reduced in thickness to approximately $\frac{5}{8}$ in. on the one mill and then transferred without reheating to a train

of three four-high mills in tandem where it is reduced to the final thickness of 0.1 in.

Whichever variation is adopted, the first mill must have large-diameter rolls (28–35 in. is usual) if it is to accept the 8–10 in. thick slabs which it is called upon to roll, and also, in the case of a two-high mill, to reduce the vertical deflections under load. Subsequent stands may have work rolls of smaller diameter, say 23–28 in., so as to reduce the rolling load, heavy back-up rolls, 50–54 in. dia., being employed to reduce the vertical deflection under load.

Normal rolling speeds with the earlier reversing stands of a hot-rolling train are up to 400 ft./min., while in the final train of tandem mills the speed may reach 1000 ft./min.

ROLL COOLING.

It will be obvious that the hot rolling of such large slabs at high outputs calls for the use of some form of roll cooling in order to ensure stable conditions, and to control the roll shape so as to obtain a satisfactory shape of blank.

The cooling is effected by means of soluble-oil sprays right across the roll barrel, these sprays often being mounted in separate banks to give control over local cambers if they should develop. Soluble oil is used because it permits the cooling efficiency of water to be used without danger of rusting the roll, and because it does contribute lubricating qualities to the roll bite. This coolant is usually circulated through a closed system with heating and cooling coils in the reservoir, so that its temperature may be kept constant within close limits.

The soluble oil also exercises a very important influence on the coefficient of friction between stock and rolls. It will be recalled that this coefficient is required to have a high value to effect heavy drafts, and rolls are usually rough ground for this reason. But in use the rolls pick up a coating of aluminium, which also increases the coefficient of friction, and the concentration of soluble oil affects the amount of pick up and therefore the coefficient of friction. If the concentration is too low, the coating thickness may increase to the point where small particles become detached and rolled into the blank; and, in an extreme case, sticking to the roll and blank cracking and tearing may occur. If, on the other hand, the concentration of soluble oil becomes too high, the coating thickness may be insufficient, and this, coupled with the increased lubricating value of the oil, may result in skidding troubles and refusals to bite, so that the draft has to be reduced. Where really high outputs are being obtained from a mill, even close control of concentra-

tion of soluble oil may be insufficient to keep the coating down, and rotary wire brushes or other means may also have to be used.

ANCILLARY EQUIPMENT.

A hot-rolling train, as described above, will carry certain necessary ancillary equipment.

A small, but important, item is the pyrometric equipment for measuring the block temperatures. It must be robust, sensitive, quick-reading, and capable of consistently high accuracy. Contact thermocouples are used with ordinary millivoltmeters for rough measurements, and with electronic amplifiers for higher accuracy.

The use of auxiliary equipment for mechanical handling has been necessitated as a result of the increased slab weights. Formerly, the stock was largely manipulated by human effort, but this is no longer possible. Special extractor machines, overhead cranes, and driven or gravity roll conveyors are used to transfer the slabs from the pre-heating furnace to the roll tables.

Edge cracking, on those alloys prone to it, is almost certainly bound up, as is shown later in the paper, with the amount of fold over at the slab edges. A recent development, therefore, is to provide vertical edge rollers immediately preceding the normal roll stand, to work the edges, and avoid the fold over.

Compressed-air jets are suitably mounted on the table to remove the soluble oil on completion of rolling, as this oil, if left on, tends to cause objectionable staining. Water-cooling sprays, followed by drying fans, may also be provided on the run-out table; cooling in this way, where applicable, saves the hold-up which would otherwise occur with air cooling, and renders the blank less susceptible to damage due to scratching in subsequent handling than it would be if hotter and softer.

As the blank leaves the last mill, the nose and tail are curved and may be folded over, the edges may be cracked or folded over owing to the manner of deformation in hot rolling, and the edges are likely to bear inverse segregates as a relic of the unmachined cast block edge. The blank must therefore be trimmed, and suitable plant is usually installed at the end of the run-off table to deal with this. A power-operated guillotine shear, mounted transversely to the rolling direction, is provided to cut off the nose and tail of the blank and to cut the blank into suitable lengths when individual sheet rolling is to be carried out to effect the final cold reduction. Where subsequent strip rolling is planned, the sheared nose of the blank is fed forward through side guides to rotary knives which trim off the edges and cut the edge scrap into pieces of suitable size for remelting.

Cold rolling on the strip mills is usually done from coils, the coil form being dictated by ease of transport, space requirements, and ease of applying controlled front and back tensions. The last item of ancillary equipment on the hot-mill line is therefore an upcoiler to form the flat blank into a compact coil.

SUMMARY OF PROCEDURE.

To summarize, therefore, the modern practice of hot rolling light alloys consists of:

- (i) "Homogenizing" of the cast slab where necessary.
- (ii) Preheating to the maximum permissible temperature, with minimum temperature gradients in the slab as delivered to the mill.
- (iii) Mechanical conveyance of the slab to the mill table.
- (iv) Cross rolling to width on a two- or four-high mill, using maximum drafts.
- (v) Turning through 90° and longitudinal rolling to (a) blank gauge, say 0.200 in., using maximum drafts, or (b) to a thickness, determined by considerations of plant balance, suitable for transfer to a four-high hot mill. This thickness is usually 3-5 in.
- (vi) Reheating to the initial hot-rolling temperature. (Not always done.)
- (vii) Longitudinal rolling with maximum drafts on the four-high hot mill to (a) a blank gauge of, say, 0.200 in. or (b) to a thickness (usually 0.4-0.75 in., governed largely by plant balance), suitable for further hot rolling on a continuous tandem train.
- (viii) Longitudinal hot rolling on a 2-5 stand continuous train to a finished gauge of, say, 0.100-0.125 in.
- (ix) End shearing, edge trimming, and upcoiling of the blank, either at 0.200 in. off a two- or four-high mill, or at 0.100 in. off the continuous train. Where a continuous train is in use, however, end shearing and edge trimming are sometimes done in addition, before entering that train.

SOME PROBLEMS OF HOT ROLLING.

While it would be false to leave any impression that hot rolling is a persistent source of many troubles, it would be equally fallacious to present it as a process incapable of improvement, or as one devoid of occasional tribulation. Crocodiling, although of decreasing incidence, can still cause serious losses in certain alloys, when it does occur. The same is true of "cradling"—a term describing a sudden upward curl

of the blank, which may damage plant and be impossible to flatten, or, at the least, causes considerable trouble in flattening. Edge cracking is satisfactorily dealt with by edge trimming; but its continued acceptance means the acceptance of quite appreciable scrappage. Further, for reasons which are gradually becoming clearer, the edge cracking may suddenly penetrate deeper into the blank, thereby occasioning further losses and dislocation of the production programme.

The rolling of 99.7% purity cover plates on to slabs of the Duralumin type, to increase the corrosion-resistance of the finished sheet, presents some problems. It is common for part of the cover plates to be rolled off in the early hot-rolling passes, the rolled-off parts ultimately detaching themselves as strips at the slab edges. Thus, further undesirable scrappage is incurred, and in addition, precise control is required if the cladding on the finished sheet is to have a uniform thickness.

The need for close control of hot-rolling conditions as affecting response to annealing, grain-size, and directionality has been mentioned earlier in the paper.

It will be clear, therefore, that the exact nature of, and the factors involved in, the deformation that occurs in breaking down are of direct importance to the practical roller. Much remains to be done before the picture is complete and precise, but sufficient is known to present an outline of the fundamentals, and this is done in Part II of the present paper.

II.—THE DEFORMATION PROCESS.

When a slab of aluminium is rolled, it is deformed in compression, the mechanism of the process being very similar to the simpler case of compression between parallel plates. The deformation which takes place during compression between parallel plates may be either homogeneous, when the plates are smooth and there is no friction between them and the metal, or it may be inhomogeneous, when the plates are rough. In the case of homogeneous deformation a straight line in the metal normal to the compressing plates remains straight and normal to the surface throughout the process, and the metal spreads laterally in a uniform manner as its thickness is reduced. On the other hand, with rough plates, such lateral spreading of the metal in contact with the compressing plates is prevented, so that the unsupported sides of the metal are bulged outwards and a line, initially straight and normal to the surface, becomes bent in the manner shown in Fig. 1. During such compression the metal within a cone of angle θ , where $\theta = \tan^{-1} \mu$ and μ is the coefficient of friction, shown shaded in the Figure, is under the

frictional restraint of the compression plates and is prevented from deforming. The coefficient of friction is therefore a most important factor, determining the kind of deformation that takes place.

The coefficient of friction between the metal and the rolls, and hence the amount of roll-face slip, depends upon the conditions of lubrication. During cold rolling, where the roll face is bright and lubrication is efficient, the coefficient of friction is low ($\mu = 0.1$ or 0.2), and it is probable that a high proportion of roll-face slip takes place, so that deformation is substantially homogeneous. On the other hand, with hot rolling under conditions of soluble-oil lubrication, the roll face becomes coated with metallic aluminium, and all the evidence suggests that no roll-face slip occurs.

The mode of deformation of the metal can be shown experimentally by studying the changes in shape of a line normal to the major faces of the rolling slab during the course of the hot-rolling process. This was done in a series of experiments carried out on commercially pure aluminium some years before the war. A number of rolling slabs $6\frac{1}{4}$ in. thick were drilled through in a direction normal to the major faces at points on the centre line distant 3 in. from each end of the block. Lengths of wire in an alloy of aluminium with 2% copper were inserted in these holes and peened over at the surface to hold them in position.

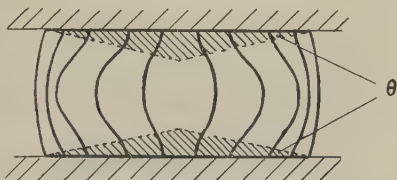


FIG. 1.—Compression Between Rough Plates.

After rolling, the ends of these wire inserts could be seen on the surface of the blanks. The latter were sectioned in a direction parallel to the direction of rolling in a plane normal to the surface and passing through the visible ends of the wire insert. The sections were then carefully milled until the plane of the section passed as nearly as possible through the axis of the wire, and finally polished.

Macro-etching followed, the procedure adopted being 3 minutes' immersion in $12\frac{1}{2}\%$ caustic soda solution followed by 2 min. in 10% hydrofluoric acid. This brought up the macrostructure and at the same time blackened the wire inserts, so that they showed up well against the pure aluminium background.

It is the normal practice, at any rate in the earlier stages of hot rolling aluminium, to use a reversing mill, so that in successive passes the stock goes through the mill in opposite directions. However, the mechanism of deformation can be more readily understood if we first

consider what happens in unidirectional rolling, such as obtains in non-reversing mills, where the stock is returned over the top of the mill after each pass.

Figs. 2-4 (Plates LV and LVI) show what happens to the shape of the wire insert in such circumstances.

It will be seen that as rolling proceeds the centre of the wire insert becomes more and more bowed in a backward direction, whilst the portion of the wire immediately adjacent to the surface remains approximately normal to the surface of the metal or is even inclined slightly forwards. The extent of the bowing becomes very considerable in the later passes, and it was found impossible to prepare a satisfactory section after the final pass, as the wire was spread over such a very great length.

Another point worthy of note is that the top and bottom of the wires do not remain in the same vertical plane as rolling proceeds, the upper end of the wire moving relatively nearer and nearer to the leading end of the blank, while the lower end moves in the opposite sense. As a result, a perceptible stagger is developed; this stagger is in the same sense at both ends of the blank, but is greater at the leading than at the trailing end.

The actual magnitude of these two effects can be seen from Table I, in which the figures given for the stagger are the measured distances, in a horizontal plane, between the two ends of the wire insert, while those for the bulge are measured from its apex to the mean position of the two ends.

TABLE I.—*Stagger and Bulge in Hot Rolling Aluminium.*

Pass	Thickness, in.	Stagger, in.		Bulge, in.	
		Leading End	Trailing End	Leading End	Trailing End
0	6½
1	5	0.15	Not measured
2	3.35	0.86	Nil	0.57	"
3	2.30	0.90	0.20	1.21	1.60
4	1.44	2.18	0.48	2.59	3.22
5	0.84	2.57	1.20	4.68	5.92
6	0.45	5.00	2.00	8.87	Not measured
7	0.25	10.8	Not measured	22	"

The figures given in the Table indicate that in this unidirectional rolling experiment the wires had rotated to such an extent that, at the leading end, the top was over 10 in. ahead of the bottom, while both were over 22 in. ahead of the centre. Such a phenomenon would suggest

that very marked concavity should have occurred at the nose end of the blank, together with a tendency for the top surface to be pulled round the corner on to the bottom. Actually no marked effect was observed, probably owing to the fact that such a tendency is not shown to any marked extent until the last few passes, when the metal is so thin that any incipient concavity would be closed up on entering the roll bite.

During rolling on a reversing mill the stock enters the rolls in opposite directions for successive passes so that much of the inhomogeneity of deformation cancels out and no considerable bulge develops in the wire inserts. It can, however, be seen in Figs. 5 and 6 (Plate LVII) that a process of alternate bending and straightening is going on. In addition to this, by alternate bending and straightening, the wire inserts are gradually rotated about an axis parallel to the axis of the rolls, the rotation being in opposite senses for the two wires so that in each case the top end of the wire gets steadily nearer to the end of the stock than does the bottom.

The extent of this can be seen from Table II.

TABLE II.—*Stagger in Hot Rolling Aluminium in a Reversing Mill.*

Pass	Thickness, in.	Stagger, in.	
		Feeding-Head End	Chilled End
0	6½
1	5	0.15	0.10
2	3.35	0.25	Nil
3	2.30	0.32	1.50
4	1.44	0.95	2.12
5	0.84	1.45	3.39
6	0.45	2.45	8.22
7	0.25	3.8	10.42

The two ends of the rolling slab were distinguished as "feeding-head end" and "chilled end" respectively, and it was arranged that the feeding-head end entered the rolls first on the odd-numbered passes and the chilled end on the even.

Thus, in this particular experiment, the upper surface of the stock was extended more than the lower during all passes, except possibly the second, the final difference being about 14 in., or about 2% on the total finished length.

Such a difference in the extension of the two surfaces must be due to asymmetry of the bite, and is presumably due to variations in the coefficient of friction between the roll face and the metal passing through the roll gap, or to variation in the angle of entry. Recent

measurements of the torque transmitted to the upper and lower rolls during the hot rolling of aluminium have shown that considerable differences can exist and that, particularly with a two-high mill such as was used in these experiments, the upper roll normally transmits the most power. Momentary ratios in power transmission as high as 6 : 1 have been noted, while at other stages in the pass the ratio has been reversed, the lower roll momentarily transmitting twice the power of the upper. For a given pass the total seems to be sensibly constant.

It is evident that during hot rolling aluminium behaves to some extent as a very viscous fluid, the pull of the rolls on the surface of the metal being communicated to the central layers by forces of a viscous nature. When the rolls bite, the surface of the metal is pulled forward at roll-face velocity, while the central layers are gradually accelerated by the viscous forces called into play.

Thus, during the first phase of the bite, the metal velocity is not uniform across a section, but steadily decreases from the surface to the centre, so that the surface of inception* is a curved surface convex to the direction of rolling.

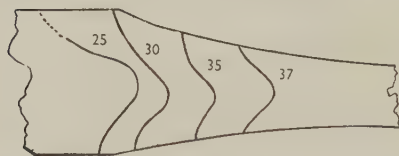


FIG. 8.—Brinell Hardness Contours in Partly Rolled Slab.

The curved form of the surface of inception can be seen from Fig. 8 which reproduces the hardness contours on a piece of partly rolled metal. These contours, being loci of points which have been worked to the same extent, should be similar in shape, if not actually parallel to the surface of inception. They show clearly that deformation of the central layers does not begin until after they have entered the bite and the surface has hardened up considerably. For light passes it is probable that the centre is worked much less than the surface. It is also interesting to note from the figures that hardening appears to begin at the surface slightly before the stock enters the rolls, and that the top surface is more heavily worked than the bottom.

The forces accelerating the central layers of the stock are, firstly, the viscous drag due to the relative movement of the various layers, and, secondly, the pressure of the metal following on behind, which, owing to the rapid constriction in the roll gap, will tend to push the metal forward. Were it not for this constriction effect it would not be possible for the velocity across any section to become uniform, which must be the case in the "zone of no slip". Here the velocity

* The surface of inception is an imaginary surface, fixed with respect to the rolls. Deformation of any particle of the stock begins as it crosses this surface.

of the metal is uniform and equal to the peripheral speed of the rolls. Beyond this point the position is reversed, the centre moving faster than the surface, which, owing to frictional restraint, continues to move with roll-face velocity. On leaving the roll gap this frictional constraint is removed, and the surface is rapidly accelerated until the velocity is once more uniform across a section, but greater than the roll-face velocity.

Observation confirms that speed at entry is less than roll-face velocity, which in turn is less than speed of exit, typical figures, in the experiments described, being 127, 174, and 194 ft./min., respectively.

In consequence of the velocity gradient between the surface and centre during the first phase of the bite, the central zones will lag behind the surface and, as shown in Fig. 9, a plane originally

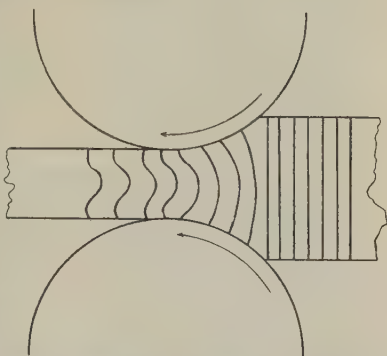


FIG. 9.—Diagram Showing Changes of Shape of Vertical Line in the Metal as it Passes Between the Rolls.

normal to the surface will become bowed backwards so that it is concave to the direction of rolling. The extent of this bowing will increase up to the point at which the velocity of the metal becomes uniform across the section, after which, as shown in the Figure, it will tend to become inverted owing to the lag of the surface during this phase. As, however, the deformation during the second phase is less than that during the first phase, this inversion will not be complete but will be confined to the surface layers.

STRUCTURAL CHANGES DURING HOT ROLLING.

During the hot rolling of aluminium of commercial purity the structure of the metal undergoes a series of changes, the original undeformed equi-axed or columnar crystals of the cast rolling block being replaced by the fine-grained and partly worked structure of the hot-rolled metal.

The earlier stages of the process, while the metal is still hot, are characterized by simultaneous deformation and recrystallization which results in a gradual breaking up of the original relatively large crystals into smaller ones without any fibre structure being developed. This process is particularly marked in the surface zones, where the deformation appears to be higher than in the centre, even with the heavy passes

used in these experiments. X-ray examination shows that with pure aluminium the surface layers recrystallize during every pass, while the central layer probably recrystallizes not more than twice or three times. This difference may be due partly to the greater deformation of the surface, which gives it a lower recrystallization temperature, and partly to the greater dissipation of energy, which raises the surface temperature above that of the centre.

The surface temperature of the metal falls throughout the rolling process, but the drop is not very rapid until the thickness is reduced below $\frac{1}{2}$ in.

In the later stages, when the temperature of the metal has fallen somewhat, the first traces of cold work begin to appear in the central region of the stock, while the surface zones still remain fully recrystallized. The structure of the metal at this stage is shown in Fig. 5 of Spillet's paper.² This structure persists until the hot rolling is completed, so that the finished hot-rolled blank has a very markedly cored structure. The central zone has a cold-worked structure with a well-marked fibre structure, in which the crystals are arranged so that they have a (112) direction parallel to the rolling direction and a (110) direction normal to the rolling plane. The surface zone has a fully recrystallized structure, but the crystals are not oriented at random; they show quite a clear fibre structure in which the (110) crystallographic directions are aligned in the longitudinal and transverse directions with a cube (100) direction normal to the surface.

This difference in degree of cold working between the surface and centre is also confirmed by hardness tests; the Brinell hardness of the centre is about 28 while that of the surface is 23, the latter figure being characteristic of the annealed material.

The experiments described above were carried out with commercially pure aluminium, and strictly speaking the conclusions which have been reached are applicable only to this material. It is, however, to be expected that the mode of deformation of the various alloys of aluminium will differ from that of the pure metal only by reason of their greater strength and different recrystallization characteristics. Thus, all that has been described above may, it is thought, be applied also to the alloys, provided due regard is given to their slightly different properties.

CROCODILING AND EDGE CRACKING.

The experiments described above were carried out with commercially pure aluminium rolled for narrow (12 in.) strip, and in consequence the passes employed were relatively heavy, several giving reductions of over

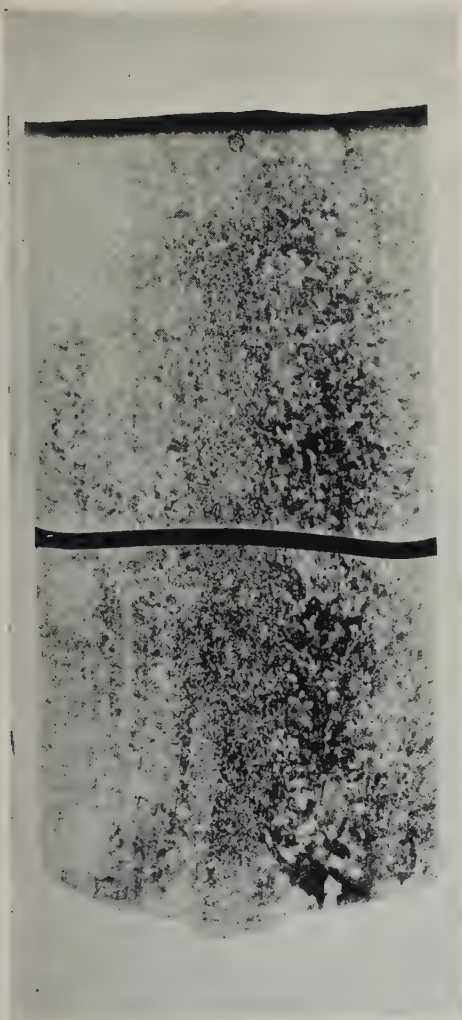


FIG. 2.—Leading End of Slab After First Pass :
Unidirectional Rolling.



FIG. 3.—Leading End of Slab
After Second Pass : Uni-
directional Rolling.

[To face p. 422.]

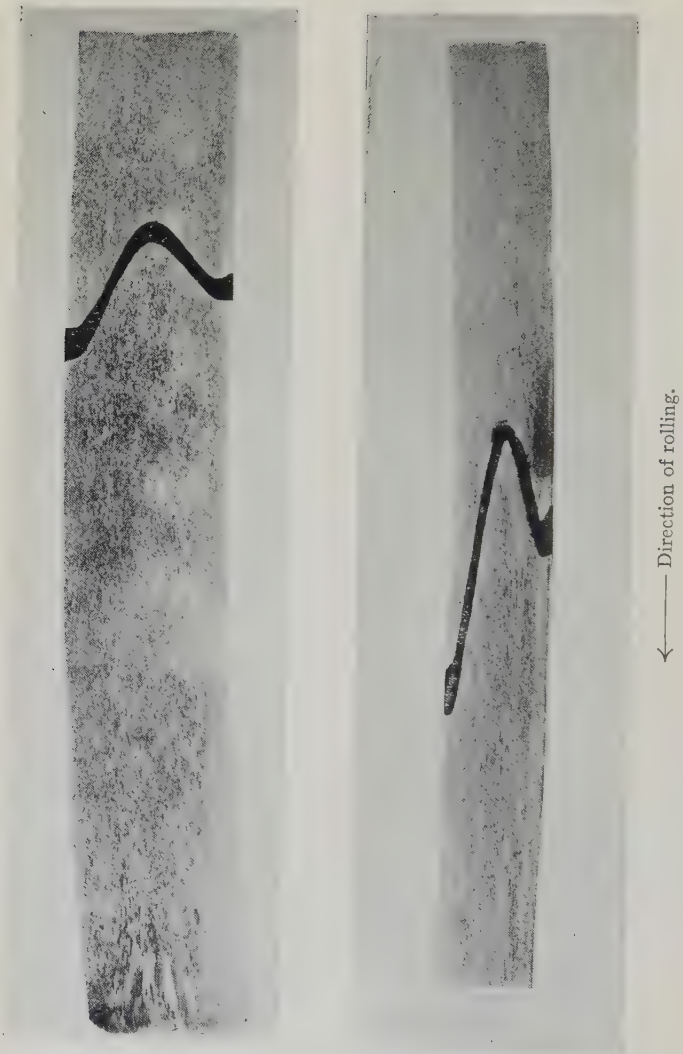


FIG. 4.—Leading End of Slab After Third (left-hand sample) and Fourth (right-hand sample) Passes : Unidirectional Rolling.



FIG. 5.—Leading End of Slab After Second Pass : Reversed Rolling.

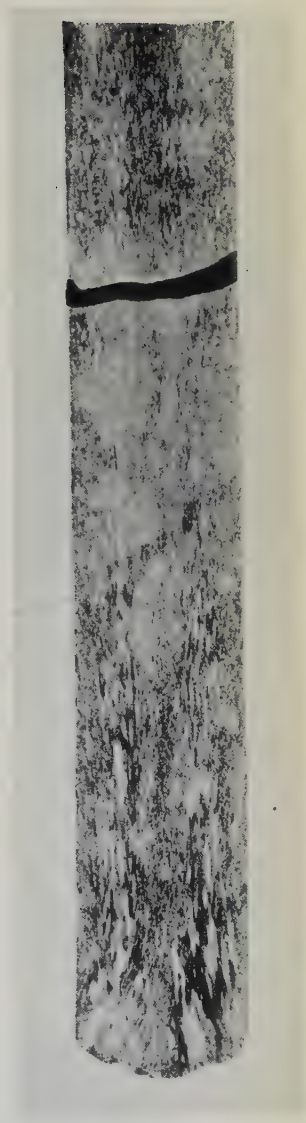


FIG. 6.—Leading End of Slab After Third Pass : Reversed Rolling.

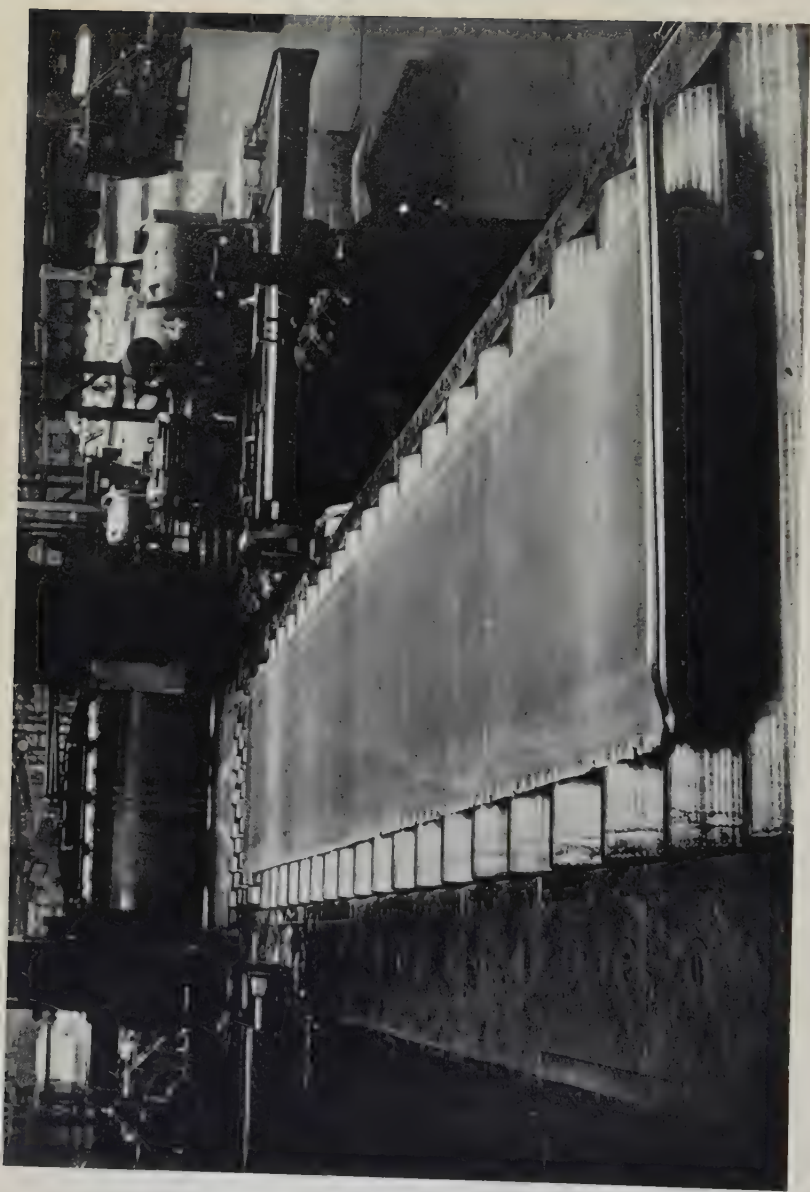


FIG. 7.—1½% Manganese Alloy, Rolled with Light Passes, Showing Edge Cracking, Concavity, and Curling.

1 in., whereas more general figures are $\frac{1}{2}$ in. for pure aluminium and 0.2–0.3 in. for strong alloys. Even so, there were clear indications that, in the initial passes, when the metal was still thick, the centre of the blank was only lightly deformed in comparison with the metal nearer the surface. With the lighter passes employed for strong alloys or wider blanks, this difference will be even more clearly marked. It was shown that even with a heavy pass the shape of the surface of inception was such that the working of the central layers did not begin until they were well inside the bite. With lighter passes and the thicker slabs now used it seems probable that the central layers are only lightly deformed until a considerable reduction in thickness has taken place.

That this is so, and that it is a function of pass intensity, is shown by the observation that an alloy slab hot rolled in 0.2–0.3 in. passes develops severe concavity at all four exposed edges. A slab of pure aluminium or 1½% manganese alloy which are given heavier passes, up to 0.5 in., while exhibiting traces of the same phenomenon only do so to a very much lesser extent, but if rolled with the same passes as used for strong alloy, they show concavity and edge cracking to an extent approaching that exhibited by the alloy (Fig. 7, Plate LVIII).

The phenomenon of crocodiling seems to be connected with these observations. With passes of about 0.2 in., it occurs most frequently at a thickness of $2\frac{1}{2}$ in., and observation shows that the concavity reaches its greatest intensity at this thickness.

This is explained if the reasonable assumption is made that deformation during hot rolling penetrates the metal to a depth of approximately three times the depth of the friction hill. With 0.2 in. passes on 34-in. rolls ($\mu = 0.4$), the friction hill on each roll is 0.4 in. deep, and at a thickness of $2\frac{1}{2}$ in. there is only a very thin layer of unworked metal between the two worked layers.

Now with such a high coefficient of friction there is a very marked tendency for the metal to stick to the rolls and be torn apart along the centre plane. If the whole of this stress is thrown on to a very thin layer of unworked or only lightly worked metal, and if the effect is magnified by the stress-raising effect of a sharp concavity, the metal will fail and the two halves open out like the jaws of a crocodile. A further contributory cause may be the occasional presence of a plane of weakness due to porosity along the central plane. As already mentioned, this is more common with chill-cast slabs.

These effects are aggravated in the case of alloys of the Duralumin type, since these alloys do not normally recrystallize during the hot-rolling operation, and the difference in properties between the worked surface and the unworked centre is therefore more marked; their

intrinsically greater hardness, and the lower rolling temperature enforced by considerations of the solidus temperature, are also aggravating factors.

The obvious remedy for this trouble, namely the use of much heavier passes, such as to cause the deformation to reach the centre of the stock at a much earlier stage in the rolling schedule, cannot in many cases be applied owing to power limitations, but there are several other palliatives which can be used effectively. In the first place, the production of a perfectly sound slab is of considerable assistance and, as mentioned earlier, it is significant that crocodiling is of much less frequent occurrence in slabs cast by the semi-continuous process than on those cast by the older methods of chill casting.

Another palliative is the use of a slab cast with a pronounced V-edge and the presentation of this V-edge to the rolls during the hot-rolling process. This is very effective, as it neutralizes the tendency to concavity and eliminates the resulting stress concentration. Finally, the introduction of two-stage hot rolling is also effective, probably because, as a result of the reheating, the temperature of the metal is some 40°–50° C. higher at the critical point than it would be in the absence of reheating, so that the ductility of the metal in the stressed zone is higher and its strength is not so inferior to that of the surface layers.

An alternative explanation was put forward by Hessenberg during the discussion of Thomas and Fowler's paper³ in October 1949. He drew attention to some work by Baker and his colleagues⁴ on residual stresses after cold rolling. These workers showed experimentally that after cold rolling the internal stresses in the metal were such that the surface layers were in tension, so that, if a plane of weakness existed down the centre line, crocodiling was the natural result.

It seems unlikely that this mechanism can operate during the hot rolling of aluminium alloys, as, except in the later stages, the temperature of the metal is above that at which rapid relief of any internal stress takes place.

The severe edge cracking which is a marked feature of the hot rolling of strong alloys appears to be connected with this same concavity, which is apparent not only at the leading and trailing edges of the stock, but, owing to the effect of widening passes and of side spread, on the side edges as well. The necessity for the use of widening passes in the initial stages of hot rolling arises when a narrow slab has to be rolled for wide sheet. The use of a narrow slab may be enforced by casting difficulties which occur generally with just those alloys prone to edge cracking. As can be readily seen, the overlapping portions of the concavity, being unsupported, do not themselves get worked during their passage

through the rolls, but they must accommodate themselves, by stretching, to the extension of the rest of the stock. The elongation required will exceed that of which the material is capable when unsupported and edge cracking will take place. Normally, the more ductile materials, such as pure aluminium and $1\frac{1}{4}\%$ manganese alloy, do not show edge cracking, but can be made to do so by hot rolling with specially light passes such as are used for strong alloys.

It is again difficult to apply the obvious remedy of heavier passes, and as it does not seem possible to cast a slab with four V-edges, the most promising solution seems to be the introduction of edge rolling, which by preventing side spread and eliminating the consequential concavity should ensure practically uniform deformation across the width of the stock.

CLADDING.

The production of strong alloys clad with a layer of high-purity aluminium on each surface is accomplished by hot rolling the slab with cover plates of high-purity aluminium in contact with its machined major faces. The process is one of pressure welding and, as has been shown by Tylecote,⁵ a certain amount of deformation at the interface is necessary before welding takes place. For pure aluminium at the hot-rolling temperature this is approximately 25–30%, and it is usually accomplished in the first two or three passes. The relative thickness of the slab and cover plate is such that during the earlier passes most of the deformation is concentrated in the cover plate. Two alternative procedures are possible; either the cover plate is made initially smaller than the slab so that this early preferential deformation extends it to the correct dimensions, or, if the cover plate initially fits the slab, it will extend until there is an appreciable overlap, which, as rolling proceeds, eventually breaks off. In this case the cladding thickness in the finished sheet is less than that calculated from the relative thicknesses of block and cover plate. Further, if the coefficient of friction for the two rolls is different, then the cladding thickness may well differ on the upper and lower surfaces of the finished sheet.

With the sizes of slab at present in use the cover plate is usually about $\frac{1}{2}$ in. thick, to give a 5% cladding. If thicker cover plates had to be used, either because of an increase in slab thickness, or to obtain a thicker cladding, then some difficulty might be experienced, as welding would not take place until the deformation had penetrated well beyond the interface between the slab and the cover plate.

EFFECT OF SLAB STRUCTURE.

Even with aluminium of commercial purity, in which recrystallization takes place continuously during the hot-rolling process, much of the cast structure of the original slab is transmitted to the final sheet. W. K. J. Pearson (unpublished work) has shown that a single crystal of the original slab may retain its identity through several successive recrystallizations. The crystal is heavily deformed and changed in shape during the rolling process, but the new and smaller crystals which grow within its boundaries as a result of the recrystallization process all have similar orientations, the mean orientation being related to that of the original crystal. The same thing occurs with neighbouring crystals, so that there is quite a sharp change in orientation on crossing one of the original boundaries. This can be revealed by etching, for sheet rolled from a coarsely crystalline slab has a streaky appearance, due to the differing directional reflectivities of the etched surface, while sheet from a fine-grained slab presents a uniform appearance due to the more random orientation of the crystals.

Pearson has also shown that this failure of the hot-rolling process to destroy completely the original cast structure is responsible for otherwise inexplicable variations in the directional properties from point to point in the sheet, and has correlated such variations with the macrostructure of the slab.

CONSTITUTIONAL EFFECTS.

In general a rolling slab of either commercially pure aluminium or of one of the alloys is not in structural equilibrium, and the process of reheating followed by hot rolling causes constitutional changes in the metal which tend to a closer approach to equilibrium. Thus, in commercially pure aluminium, which is, strictly speaking, a ternary alloy of aluminum, iron, and silicon, the slab, particularly if cast by the semi-continuous process, has more silicon retained in solid solution than the equilibrium amount at the rolling temperature, and in addition the peritectic reactions resulting in the conversion of FeAl_3 to $\alpha(\text{Fe-Si})$ and then to $\beta(\text{Fe-Si})$ will only have proceeded to a relatively small extent. Thus, during the preheating operation and also during the actual hot rolling, silicon will be precipitated, and much of the tough FeAl_3 and $\alpha(\text{Fe-Si})$ will be converted into the more brittle $\beta(\text{Fe-Si})$ phase.

Other alloys behave similarly. In particular, in the alloy with $1\frac{1}{4}\%$ manganese, so much manganese is retained in solid solution after semi-continuous casting (the solubility at the eutectic temperature is about 1.8%), that although some precipitation takes place during normal

preheating, a homogenization treatment of about 12 hr. at 570° C. is necessary in addition, in order to reduce the amount of manganese in solid solution to such a level that recrystallization can take place at reasonably low temperature, and also that a fine grain may be obtainable on annealing. With other alloys, notably those containing magnesium, homogenization may also be desirable in order to minimize the coring effect. Such alloys, in which there is a very long range of solid solution at the eutectic temperatures, solidify in such a manner that the amount of magnesium in solid solution varies from almost nothing at the centre of each crystal to nearly 15% at its boundary. The removal of such a concentration gradient by a homogenization treatment has a marked effect on the ductility of the alloys and therefore improves the ease of hot rolling.

Additionally to the above, the "kneading" of the metal at the rolling temperatures is a powerful influence in favour of the approach to structural equilibrium and does much to raise the effective solidus of alloys of the Duralumin type from 506° C. towards its equilibrium value of 515° C., thus permitting them to be heat-treated at the temperatures normally employed for such alloys as D.T.D. 610B.

Effect of Breaking-Down Temperature on Grain-Size.

Phillips⁶ has shown that the temperature of hot rolling has a very strong effect on the grain-size of the annealed sheet, the higher the hot-working temperature the finer being the grain-size after annealing. This appears to be due to the greater proportionate conversion of the tough FeAl_3 to the more brittle $\beta(\text{Fe-Si})$ phase at the higher temperatures. The $\beta(\text{Fe-Si})$ phase is broken up during the hot rolling and subsequent cold rolling, and the increased number of particles offers greater mechanical obstruction to grain growth on annealing.

From this point of view, therefore, it is clearly desirable to employ the highest practicable temperature for hot rolling.

Effect of Breaking-Down Temperature on Rate of Annealing.

Another effect of hot-rolling temperature which appears to be of a constitutional nature is its effect on the rate of recovery and recrystallization. Commercially pure metal hot rolled at temperatures above 500° C. is much more sluggish in its response to annealing than is metal hot rolled at lower temperatures.⁷ That this effect is a constitutional one is shown by the fact that, firstly, no such difference can be detected with super-purity aluminium, the response of which to annealing is independent of the rolling temperature, within the limits 20°–550° C., and also that it is largely removed by a process anneal.

Effect of Breaking-Down Temperature on Directionality.

In addition to the effect of the hot-rolling temperature upon grain-size and upon annealing behaviour, there is yet another effect of practical importance which is thought to be of constitutional origin. Unpublished work by W. K. J. Pearson and independent observation by A. E. Musgrave have shown that sheet produced from commercially pure aluminium hot rolled at temperatures in excess of 500° C. differs from that rolled at lower temperatures in its recrystallization texture. The recrystallization texture of metal rolled at high temperatures is of the (112) type common to cold-rolled aluminium, so giving ears at 45° to the direction of rolling. That of metal rolled at the lower temperatures is of the cube type and gives ears at 0° and 90° to the direction of rolling.

As in the case of the other constitutional effects, this cannot be detected with super-purity aluminium, and it also is eliminated by the introduction of a process anneal.

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THE EXTRUSION OF ALUMINIUM ALLOYS.* 1226

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SYNOPSIS.

The extrusion process is described, with special reference to its use for aluminium alloys. Some information is given on the practice employed in die manufacture, and the nature of the flow that normally occurs in the extrusion of non-ferrous alloys is briefly considered. The particular conditions which may arise in the extrusion of aluminium alloys are described, and the dependence on these conditions of the type of structure and properties obtained is discussed. Problems associated with the production of heat-treated alloys in the form of extrusions are also dealt with.

I.—THE EXTRUSION PROCESS.

THE extrusion of non-ferrous alloys has been dealt with by a number of workers. Genders¹ has described the extrusion of copper-base alloys, and a very detailed account of the production of extrusions in various non-ferrous alloys is contained in Pearson's book.² An interesting description of the mode of flow of aluminium alloys in extrusion has been given by Walbert,³ and an informative account of the technique of extrusion of aluminium alloys has recently appeared in *Alluminio*.⁴

The process in universal use for the extrusion of aluminium alloys is that known as the "direct" process. The steel die, in which is cut an aperture of the shape of the required product, is located at one end of a heated cylindrical steel container. A cylindrical billet of the alloy, cut to a suitable length, and of a diameter as near as practicable to that of the container, is heated to the correct temperature for extrusion and placed inside the container. A heated steel plate (called a follower plate) is placed at the end of the billet remote from the die. Pressure is then applied to the follower plate by a hydraulic ram, and the heated metal is forced through the die, assuming the shape of the orifice as it emerges. Thus the energy is transmitted through the billet being extruded. A considerable amount of this energy is used up in overcoming friction, and is dissipated as heat, while the remainder serves to deform the cylindrical billet into the required shape.

Hollow extrusions are produced from hollow billets, in the bore of which a mandrel is inserted. Such mandrels may be loosely fitted into

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the follower plate, or screwed in the end of the extrusion ram. In both cases the mandrel moves forward slowly as extrusion proceeds, and the form of the annulus between the mandrel and the die determines the shape of the product extruded.

A recent innovation for the production of hollow shapes is that in which ante-chamber or bridge dies are used in conjunction with solid billets. In this process pressure welding is involved.

Presses may vary in capacity from 500 to 6000 tons; a 500-ton press would normally be used for the extrusion of rods up to about $\frac{3}{4}$ in.² sectional area from billets about 3 in. in dia., and a 6000-ton press for sections approximately 35 in.² from billets of 20 in. dia.

II.—BILLETS FOR EXTRUSION.

In modern plants the cylindrical billets used for extrusion are cast semi-continuously, and such billets have structures of a fineness and soundness which have resulted in slight but measurable improvements in the mechanical properties of extrusions as compared with those of extrusions produced from chill-cast billets. One of the difficulties associated with the use of semi-continuously cast billets lies in the development, in some alloys, of marked surface exudations consisting of various eutectics present in liquid form in the last stages of solidification. These are most apparent in the alloys containing copper, but even in the most difficult cases effective control of them may be exercised in billets up to about 5 in. dia. by paying attention to the pouring temperature and speed used and to the depth and contour of the moulds. In the larger sizes of billet, such as those 12, 16, or 20 in. in dia., very marked solidification shrinkage occurs during the passage of the metal through the mould, so that an air gap between the billet surface and the mould wall of quite considerable proportions exists, permitting the development of exudations which project considerably from the true billet surface and have to be machined off before extrusion. The production of large billets for extrusion is an interesting problem in itself, but this does not lie within the scope of the present paper.

III.—PREHEATING THE BILLETS.

Extrusion billets are normally preheated in electrically-heated furnaces, though both gas- and oil-fired furnaces of suitable design are also used successfully. The electric furnace is to be preferred, since it may be accurately controlled and gives a satisfactory furnace atmosphere. Alloys of the aluminium-magnesium type should not be preheated in gas- or oil-fired furnaces unless they are of the true muffle

type, since the products of combustion may react with the alloys to the detriment of their welding characteristics. All furnaces for preheating should admit of precise temperature control in order to ensure the best quality of extruded product, a working range of $\pm 10^{\circ}$ C. being advisable for most operations.

For some alloys, it is necessary to use very prolonged preheating times in order to homogenize the structure. In such cases preheating periods as long as 24 hr. may be required, but for normal purposes 4 hr. is usually sufficient.

IV.—EXTRUSION DIES.

The manufacture of dies for extrusion demands considerable experience, if consistent results are to be achieved. For regular shapes such as rounds, squares, and rectangles, where the flow of metal is more or less uniform, the problem is not a difficult one. Fig. 1 is a sketch of the cross-section of an extrusion die suitable for the production of 1-in. round bar. The arrow indicates the direction of extrusion. It will be observed that the edge of the die orifice in contact with the billet is relatively sharp, deformation of the alloys being effected by shear. The function of the bearing of the die is of great importance when irregular shapes and shapes of greatly varying cross-section are being produced. In such cases a longer bearing has to be used to check the flow of metal in the thicker areas. This is illustrated in Fig. 2, in which the disposition of the bearing is clearly seen. The flow of metal may also be checked locally by applying a radius to the sharp edge of the relevant part of the die. It is important that the die be well polished and sharply backed out in order to achieve bright surfaces free from die-lines and "pick-up".

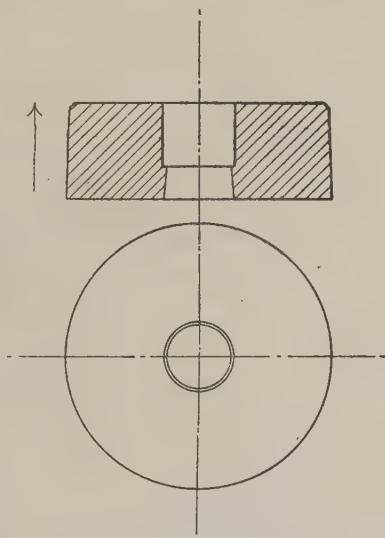


FIG. 1.—Extrusion Die for Round Bar.

A variety of die materials is available, including tungsten steels and low-alloy steels; although in certain instances dies made from hard and brittle materials such as Stellite and cemented carbides have been

used, they have by no means replaced steel dies. Dies fail either by slow collapse or by cracking, particularly at sharp corners, and the efficiency of the extrusion process is naturally improved by careful attention to the hardening and tempering of the die materials and to the details of design of the extruded shapes. During extrusion, the dies attain temperatures of about 350°C . and may be subjected to pressures as

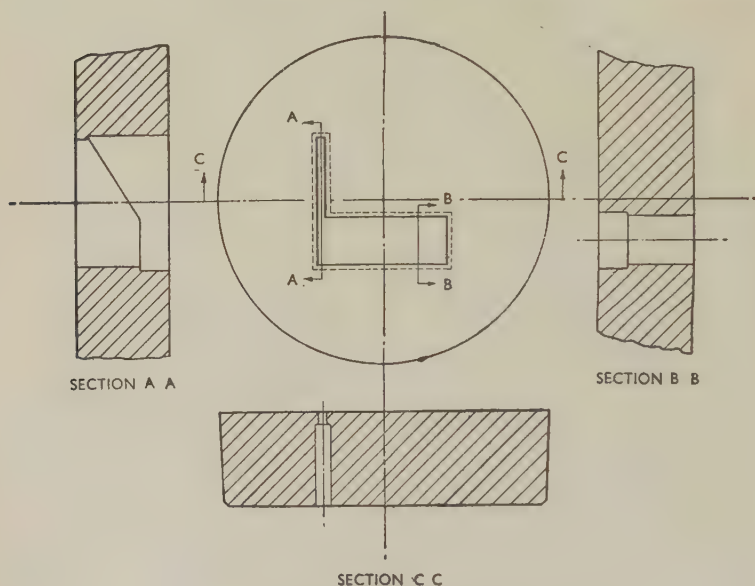


FIG. 2.—Extrusion Die for Irregular Section.

high as 50 tons/in.², so that local stresses in them may be much higher than this.

Press containers are heated by electrical-resistance heaters, and in some cases also by town's gas, and container temperatures are of considerable importance in their relation to the structures and properties of extrusions. Induction heating is also used, but has not found good favour.

V.—METAL FLOW IN EXTRUSION.

When a heated billet is placed in the container there is, of course, a clearance between the two. On the application of pressure, the billet is squeezed up, and practically fills the container before any extrusion begins. Owing to the friction between the billet and the die at one end

and the billet and the follower plate at the other, the billet retains its original diameter on the cut faces, so that the corners of the container fill up slowly as extrusion proceeds.

During extrusion, flow occurs most rapidly at the centre of the billet. Owing to the restraining effect of the die face, and the frictional effects between the curved surface of the billet and the container wall, the outer zones of the billet resist deformation, and shear forces are set up in the heated billet. The location of these forces may be indicated fairly accurately by curved lines drawn from the perimeter of the die orifice to the perimeter of the back of the billet. As the billet shortens, the angle included by these lines becomes more obtuse, and the shear forces increase materially. Finally, owing to the different rates of flow within the billet, it becomes hollow, and if the extrusion ram is allowed to go too far, defects in the form of surfaces of separation appear at the centre of the extruded section, and are known as "pipe" or "the extrusion defect". In order to prevent this, it is customary to leave in the container a discard whose length is 10 or 15% of the original length of the billet. It should be made clear also that the follower plate is deliberately made of slightly smaller diameter than the container so that a liner of aluminium alloy in intimate contact with the container surface remains behind. This contains the oxide which was present on the surface of the billet, and it is removed when another follower plate or "cleaner" of larger diameter than the ordinary follower plate is subsequently passed through the container.

The method of flow has been described and illustrated many times by the use of composite billets, by means of models made of parti-coloured Plasticine, and in other ways, but its effect on the structure of extruded sections in aluminium alloys, particularly those which have to be subsequently heat-treated, has perhaps been fully appreciated only by those responsible for the manufacture of these products.

In most hot-working processes the material being worked is subjected to fairly uniform deformation, and it is possible, within limits, to produce a finished or semi-finished product of reasonably uniform structure. There are exceptions to this generalization, as there are in the case of forging, where acute variations in grain structure may appear near flash areas. In extrusion it is difficult, particularly with alloys having a high recrystallization temperature, to obtain structures which are uniform, owing to the special conditions arising during the process.

Fig. 3 (Plate LIX) illustrates the macrostructure of an aluminium alloy billet which has been extruded one-third of its length. The effects of the friction of the curved surface of the billet against the container

wall may be observed in the intensely local flow at the surface, and it is also apparent that the metal in the front corners of the billet adjacent to the die is taking no part in the flow. Fig. 4 (Plate LIX) shows the macrostructure of a billet similar to the above, which has been extruded 80% of its length. The restraining effect of the container assembly now becomes clearly apparent, for the metal in the corners of the billet adjacent to the die is still undisturbed, and microscopical examination shows that the structure here is still substantially as cast (Fig. 5 (a), Plate LX). Fig. 5 (b) shows the microstructure at a position opposite the die orifice. The metal in this zone has already been drawn out longitudinally, and both the grains and the clusters of compounds show considerable directionality.

Reverting to Fig. 4, the photomacrograph of a billet extruded 80% of its length reveals an annular zone, of roughly elliptical cross-section, in which an obvious disturbance of the structure has occurred. It is the conditions giving rise to this zone which present most of the problems associated with the production of aluminium alloy extrusions. From consideration of the method of flow already described, it will be realized that the metal in this area is subjected to very heavy shear stresses during extrusion. These stresses increase in magnitude from the centre outwards, and reach a maximum at the limit of the unextruded metal in the corners. The conditions existing near to the line of demarcation visible on the outer edges of this zone (see Fig. 4) may be compared with those at the site of a geological fault; indeed, in some extreme cases, complete separation of the metal by shear occurs, while in others minute and localized shear slitting may arise. This analogy must not be carried too far, since heated metals are plastic materials, but there is one phenomenon in aluminium alloy extrusion which is common to the two processes, and this is the development of local heat. During the conversion of an aluminium alloy billet into an extruded section a considerable amount of heat is developed. Much of this heat is, of course, dissipated, as the tools in contact with the billet are normally cooler than the latter, but owing to the intense local shear effects described a restricted zone develops in which a very considerable increase in temperature occurs. With certain alloys having solidus temperatures just above 500° C. incipient fusion may actually occur during extrusion. In a similar way, the melting of rock takes place during the development of a geological fault, with the formation of gneiss. In alloys having low solidus temperatures this condition may occur more frequently than is generally realized, and it is sometimes possible to detect, by careful microscopical examination, an exceedingly local area just below the surface of the extrusion, which

contains chilled liquid. Tensile tests of such materials show them to have normal strength and ductility.

The preceding discussion indicates that the temperature factor in extrusion is important, and that the whole problem is somewhat complex. It is further complicated by the fact that in many extruded products certain areas of the extruded section may be completely recrystallized, while other areas may not. In cases where the sections have subsequently to be heat-treated, this condition may lead to further effects. These can be illustrated by examining the crystal structures of billet discards which have been subjected to heat-treatment. It is realized that an examination of discards in this way may not reveal exactly the type of structure obtained in the extruded product from the particular billet being examined, and cross-sections of the actual extrusions produced from the same billets, also heat-treated, are illustrated. Fig. 6 (Plate LXI) shows the structure of two such discards. These were extruded at different temperatures and subsequently heat-treated at 505° C. The alloy in these cases conforms in chemical composition with the requirements of Ministry of Supply Specification No. D.T.D. 364B. In Fig. 6 (b) it will be seen that the metal in the area of critical strain has recrystallized, and that grains of an extremely large size have developed. In Fig. 6 (a) the metal in the critical area has not recrystallized during heat-treatment, and has retained its fine grain. The macrostructures of the extruded rods produced from these billets show in the first case that the bar has an outer annulus which consists of crystals of great size compared with those in the body of the bar, while in the second case the crystals in the outer area are finer than those in the body of the bar, which in both cases have not recrystallized. If test-pieces are cut from the areas of the bar having a large-grained annulus, it will usually be found that they have proof stresses and ultimate stresses lower than those of the material from the inside of the bar, and higher elongations. The actual test results on the bar illustrated are given in Table I.

TABLE I.—*Tensile Properties of Extruded Bar in D.T.D. 364B Alloy.*

	0.1% Proof Stress, tons/in. ²	U.T.S., tons/in. ²	Elongation, %
Centre of bar . . .	28.8	33.7	12.0
Outer annulus . . .	25.2	30.9	14.0

Fatigue test-pieces taken in similar locations do not normally show a large variation in fatigue values, but in the case of the large-grained material there is usually a much wider scatter of results.

A very wide variety of factors affects all the characteristics discussed, the chief of which are temperature and speed of extrusion, and composition. It is proposed to discuss these factors separately, although, of course, they are very much related to one another, and in practice have to be considered together.

VI.—TEMPERATURE AND SPEED OF EXTRUSION.

These factors cannot be separated. Faster extrusion speeds lead to higher temperatures, and if billets initially at high temperatures are extruded, extrusion speeds have to be materially reduced if break-up of the metal at the die bearing is to be avoided.

At first glance it might not appear difficult to steer a safe course between the danger of overheating and that of large-grain development. In the case of the non-heat-treated alloys this is largely true, for in the author's experience the development of large grain does not occur except in those rare cases where non-heat-treatable alloys have subsequently to be annealed, and these alloys are usually of the solid-solution type free from low-melting-point compounds. In addition, they usually have lower recrystallization temperatures than the heat-treated alloys.

With the heat-treatable alloys the lower solidus temperatures and the need for solution-treatment after extrusion both have to be considered. Ignoring for the moment the factor of chemical composition, it will be found that the condition most favourable to the retention of fine grain in the heat-treated product is that in which an extrusion temperature has been used sufficiently high to enable recrystallization to occur during the actual extrusion operation, or immediately after the section issues from the die. In a number of cases this temperature is found to be so high as to be impracticable, since under these conditions there is a danger of inducing incipient melting during extrusion, unless the speed is uneconomically low, and the metal is so weak as to be unable to withstand the friction of the die-bearing and breaks up. If a lower temperature is selected, a very fine balance of temperature and speed of extrusion has to be maintained if satisfactory results are to be achieved. The difficulty of the problem is intensified by the fact that in the zone of the extruding billet which gives rise to the large-grained annulus a strain gradient is left. Thus, if any strain remains in the extruded product, it is almost inevitable that in some position a degree of strain favourable to grain growth is present. This condition may be compared with those that arise in the well-known technique wherein a tapered test-piece is strained and subsequently heated above its recrystallization temperature. Somewhere along the test-piece critical conditions inevitably develop, and a local area is observed in

which exaggerated grain growth has occurred. Prolonged heating may result in a widening of this area.

It is difficult to discuss this subject in detail in all its ramifications, for each extrusion represents a separate problem. The size, shape, and length of the extruded product have to be taken into account, as they cannot be changed and hence impose certain limits to what can be achieved in the way of temperature variation. In one case, for example, fine grain was achieved in a heat-treatable alloy of the Mg_2Si type by a marked increase in the extrusion speed. In other cases, control of the container temperature within fairly narrow limits has given satisfactory results. The conditions existing during extrusion are a composite of alloy composition, billet temperature, tool temperature, container temperature, size and length of extruded product, and extrusion speed. With so many variables involved, it is evident that a precise control, in which a given set of conditions is faithfully reproduced, is difficult. As will be discussed later, the heterogeneity of the cast billet is also a very important factor, since it materially affects the recrystallization characteristics.

Depending on the alloy and the extrusion conditions obtaining, it is therefore possible for extruded products to be unrecrystallized, wholly recrystallized, or recrystallized only in part. The factor of heat-treatment after extrusion may affect the ultimate state of the product, but heat-treated extruded sections may also be produced in the above three conditions.

The factor of extrusion pressure does not appear to have any relevance to this problem, except in so far as it affects extrusion speed or rate of straining. In alloys which do not contain elements that raise their recrystallization temperatures, a high rate of strain, permitting recrystallization to occur during or immediately after extrusion, is preferable. In such alloys the temperature of the billet and that of the container should be as high as is practicable. Under such conditions heat-treated extruded sections in alloys of the Mg_2Si type, and of the complicated D.T.D. 130 type, may be produced with uniformly fine grain.

The actual temperatures and speeds of extrusion which are most commonly used in practice can be defined only in general terms. In alloys of the copper-bearing Duralumin type the solidus temperatures are just above $500^{\circ}C.$, and, of course, the alloy becomes extremely weak below that temperature.

It is felt that a field in extrusion technique which may deserve study relates to the frictional effects of the die itself. Thus, in an ordinary extrusion press, at a temperature of $440^{\circ}C.$, B.S. 6L1 alloy may be

extruded at speeds around 6–8 ft./min. In an experimental press, using dies of a design similar to those used in industry, and extruding by a technique involving impact extrusion, speeds up to 700 ft./min. may be achieved without any indication whatever of surface cracking, and with excellent rod surfaces. It will be appreciated that this latter work was carried out on a very small scale, in a press having a container of $1\frac{1}{2}$ in. dia., with a length of 2 in. only, and that the power necessary to effect in this manner the extrusion of such an alloy in large pieces is not available. It is of interest to note that in the experimental extrusion the flow of the metal in the small container was not of the type discussed earlier, but was of the freely lubricated type experienced in the extrusion of copper tubes and described so admirably in the paper by Blazey and his co-workers.⁵

Alloys of the Mg_2Si type may normally be extruded at higher temperatures and speeds than those containing copper in significant amounts, and temperatures of 480°–500° C. with speeds of 30 ft./min. or very much higher may successfully be practised. With the pure metal speeds may be higher still.

Greater difficulty is experienced with the very strong alloys of the aluminium–zinc–magnesium type. These are normally extruded at about 420° C., and they offer considerable resistance to deformation. Up to date, these alloys are extruded at speeds of about 3–4 ft./min., and break-up occurs at slightly higher speeds. There is a critical speed at which satisfactory extrusions may be produced with these alloys, which lies within the range 40–80 ft./min. at a temperature of about 360° C. It is very unlikely, however, that such conditions would be practicable in production, as they could neither be achieved nor maintained with the type of product which is normally produced. As in the case of the experimental impact type of extrusion, however, these facts indicate that the problem of frictional effects will repay further study.

Other things being equal, it may be said that, for all alloys, the permissible extrusion speed is lower, the larger is the cross-sectional area of the extrusion. The extrusion speed has to be lower when sections have sharp corners and rapid changes of thickness, and extrusion temperatures have to be higher when the sections are of small cross-sectional area. Those alloys having a low solidus temperature and a wide solidification interval have to be extruded more slowly than those in which the solidus–liquidus range is small. Having in mind all the facts enumerated above, some diffidence is felt in giving precise sets of conditions which may be applied to the alloys normally extruded. As a general guide, however, some typical figures are set out in Table II.

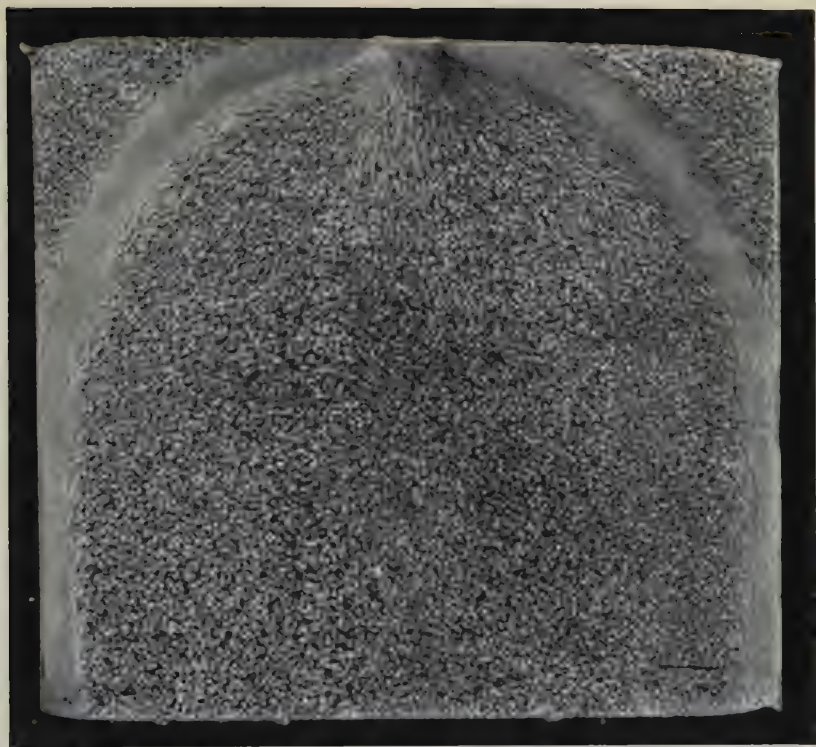


FIG. 3.—Macrostructure of Aluminium Alloy Billet extruded one-third of its length. $\times \frac{1}{2}$.

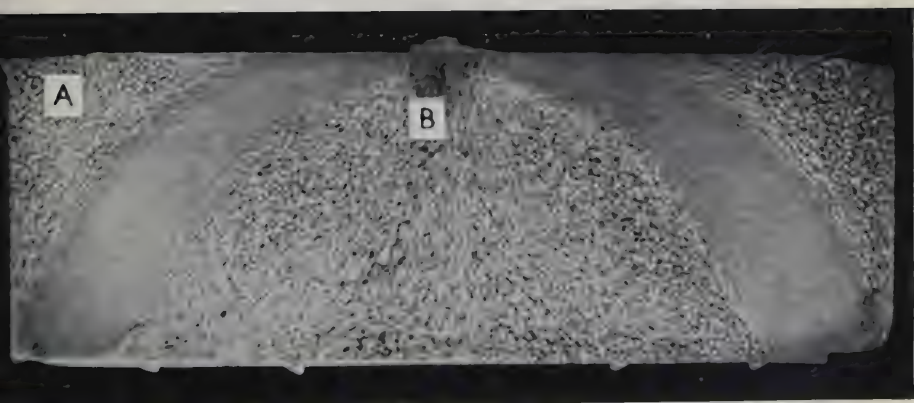


FIG. 4.—Macrostructure of Billet similar to that in Fig. 3, but extruded 80% of its length. $\times \frac{1}{2}$.
(For microstructures at points *A* and *B*, see Fig. 5, Plate LX.)

[To face p. 438.]

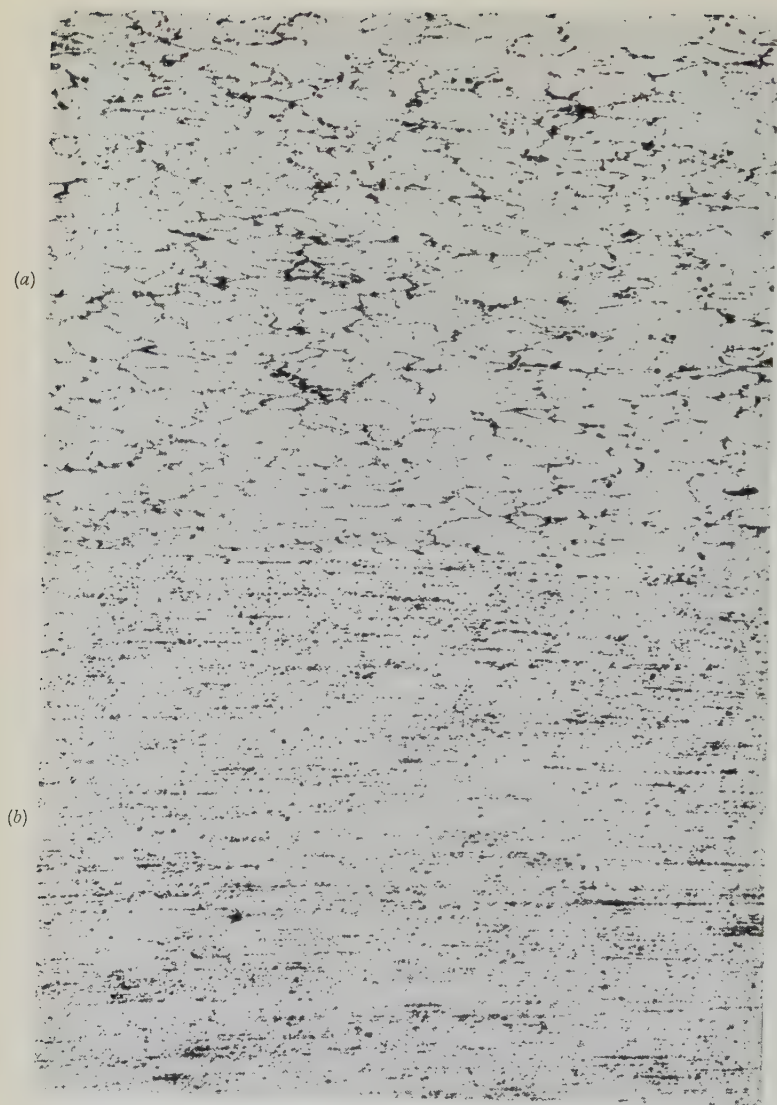
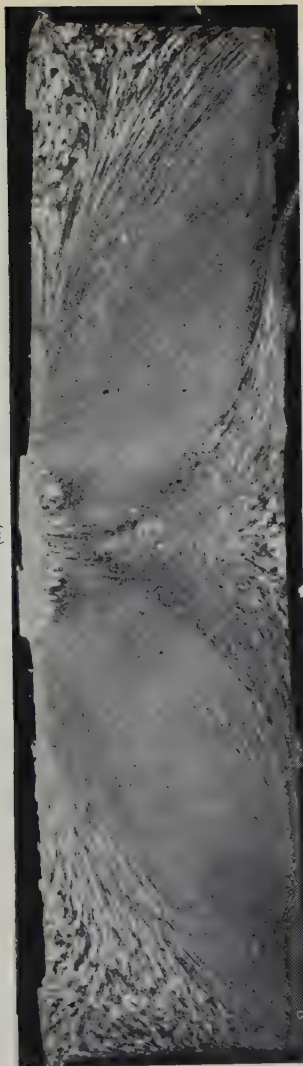


FIG. 5.—Microstructure of Aluminium Alloy Extrusion Billets (a) in corners adjacent to the die and (b) opposite the die orifice. (Points A and B in Fig. 4.) $\times 50$.

(a)



(b)

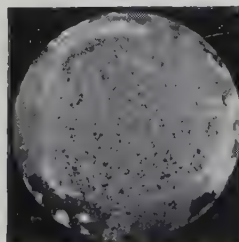
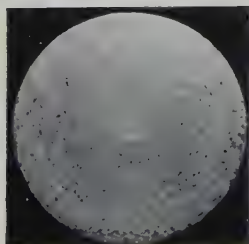
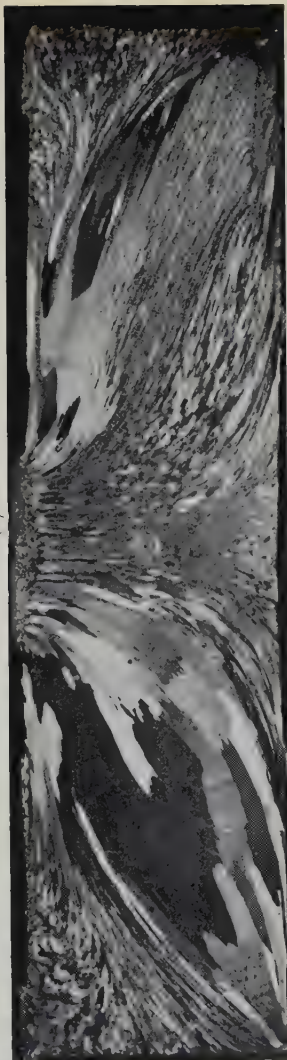


FIG. 6.—Extrusions and Discards of D.T.D. 364B Alloy Heat-Treated at 505° C. showing (a) fine grain of unrecrystallized metal and (b) coarse grain after recrystallization. $\times 1$.

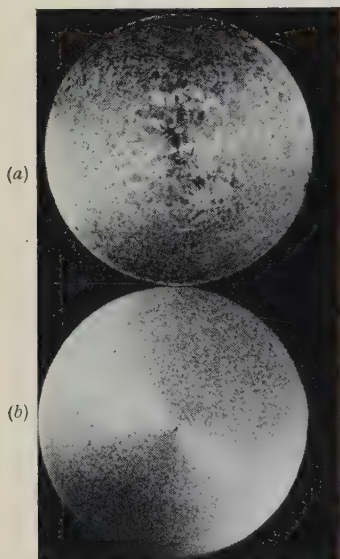


FIG. 7.—Macrostructures of Extruded Duralumin Rods Containing (a) no Mn; (b) 0.6% Mn. $\times 1$.



FIG. 8.—Extruded Aluminium Alloy Bar forged at 420°C . to a tapered shape and then heat-treated at 500°C . $\times \frac{1}{2}$.



FIG. 9.—Microstructures of 2-in.-dia. Duralumin Extruded Bar. Surfaces parallel to main axis of bar. Not heat-treated. $\times 200$.

- (a) 1 in. from front end.
- (b) 1 ft. from front end.
- (c) middle.
- (d) back end.



FIG. 10.—Macrosection of Half of a Discard, Showing Effect of Cold Shuts in Extrusion Billet.

TABLE II.—*Typical Extrusion Temperatures and Speeds for Some Aluminium Alloys.*

Alloy Composition				Extrusion Range, ° C.	Optimum Temp., ° C.	Container Temp., ° C.	Extrusion Speed, ft./min.
Cu, %	Mg, %	Si, %	Zn, %				
4	0.6	0.6	...	400–480	450	420	6–8
2	0.6	1.0	...	400–480	460	420	15–20
...	0.6	1.0	...	400–520	500	420	30–50
1	2.0	...	6.5	380–440	420	420	3–4
...	2.0	380–440	420	420	14–18
...	5.0	400–460	440	420	8–14
...	7.0	400–460	440	420	4–6

VII.—COMPOSITION.

(a) *Effect of Soluble Elements.*

General observation of the behaviour of various alloys in extrusion suggests that those alloys which contain large proportions of insoluble compounds are least likely to grow large grains on subsequent reheating. The author has not had a great deal of experience of the extrusion of pure aluminium, but is of the opinion that the pure metal, in the extruded condition, is very sensitive to reheating effects, since he has seen a number of cases in which not only the outer annulus, but the whole cross-section of quite large extrusions have developed grains of large size on reheating. Aluminium bars with a fine-grained annulus enclosing a centre of very coarse grain have also been observed. This is most unusual in the strong alloys and may be the result of the extremely low resistance to deformation of the pure metal. In a similar way the heat-treatable alloys of the Mg_2Si type, designated AW9 and AW10 in the British Standard STA7 schedule, may give difficulty owing to grain growth during heat-treatment, unless grain-growth inhibitors, or very fast extrusion speeds, are used.

Alloys of the Duralumin type, containing copper and other elements up to a total of over 6%, might be regarded as being relatively free from grain growth on solution-treatment, but a high proportion of the alloying elements are soluble at the solution-treatment temperature, and the effect of the removal of the soluble constituent during heat-treatment appears to be that there is a sudden flashing of grain growth. This has been illustrated by Beck, Holzworth, and Sperry⁶ in work carried out on an aluminium-manganese alloy.

(b) *The Extrusion Effect.*

Two elements exercise an important function on the characteristics and mechanical properties of extruded aluminium alloys, namely, manganese and chromium, and their function appears to be that of raising the recrystallization temperature of the alloys. Alloys containing manganese, on this account, exhibit what has been called the "extrusion effect".

The effect is adequately illustrated by a study of the mechanical properties of B.S. 6L1 alloy in various forms. The chemical composition of this alloy may be quoted as follows:

Cu, %	Mn, %	Mg, %	Fe, %	Si, %	Al
4.2	0.6	0.6	0.3	0.3	Remainder

In Table III are shown the mechanical properties of examples of this alloy in three forms; results obtained on an extruded bar of an alloy of similar composition from which the manganese has been omitted are also given. The materials tested were as follows:

- (a) Rolled heat-treated sheet, 0.064 in. thick.
- (b) Extruded heat-treated bar, 2 in. dia.
- (c) Forged heat-treated bar, $\frac{3}{4}$ in. dia., forged from (b).
- (d) Extruded heat-treated bar (no manganese), 2 in. dia.

The heat-treatment consisted in all cases of solution-treatment at 500° C., quenching, and ageing for 7 days at room temperature.

TABLE III.—*Tensile Properties of Duralumin-Type Alloy.*

Form of Material	0.1% Proof Stress, tons/in. ²	Ultimate Stress, tons/in. ²	Elongation, % on 2 in.
(a) 0.064 in. thick sheet . .	15.5	27.5	16.0
(b) 2 in. dia. bar (Mn) . .	20.6	33.5	15.0
(c) $\frac{3}{4}$ in. forged bar . .	14.2	25.8	20.0
(d) 2 in. dia. bar (no Mn) . .	14.1	25.1	18.0

The microstructures of these specimens showed that the samples of sheet, forged bar, and manganese-free extruded bar had recrystallized during solution-treatment, while the sample of extruded bar containing manganese had not recrystallized. Photomicrographs of the two extruded bars are shown in Fig. 7 (Plate LXII) for comparison. An experiment of a similar nature on the aluminium-zinc-magnesium type of alloy illustrates the same phenomenon. Cast billets of the composition shown in Table IV were extruded into 1-in. round bar under the same extrusion conditions, solution-treated at 465° C., quenched in water, and artificially aged at 135° C. for 12 hr. The difference in

the mechanical properties of these two bars is striking, and illustrates well the "extrusion effect", which is seen to be largely dependent on composition.

Chromium behaves in a similar way to manganese, and these two elements have assisted materially in the production of extruded alloys

TABLE IV.—*Composition and Properties of Two Aluminium-Zinc-Magnesium Alloys.*

Alloy	Cu, %	Mn, %	Mg, %	Zn, %	Fe, %	Si, %	Al
A	1.78	0.58	2.53	4.82	0.4	0.2	Remainder
B	1.85	0.07	2.62	4.97	0.36	0.19	Remainder
	0.1% Proof Stress, tons/in. ²		Ultimate Stress, tons/in. ²			Elongation, % on 2 in.	
A	34.1		36.4			6.5	
B	30.4		34.8			15.0	

of extremely high strength. It follows, from these facts, that the very high tensile strengths of over 40 tons/in.² frequently obtained on extruded sections, cannot be obtained on either sheet or forgings.

Readers of specifications for extruded aluminium alloys may have been intrigued by the frequent allusion in those documents to "sections thinner than $\frac{3}{8}$ in.", for which mechanical properties about 1 ton/in.² lower than those of thicker bars are specified. This difference is due to the fact that even with the customary addition of elements which tend to inhibit recrystallization, the thinner sections, which are more highly strained, do in fact recrystallize on heat-treatment across their whole cross-section, with consequent loss of the "extrusion effect".

The effect of grain-growth inhibitors is more marked in the case of the aluminium-zinc-magnesium alloys, and in this field the effect of chromium in addition to manganese is helpful. With these alloys the function of the inhibitors is facilitated by the fact that the solution-treatment temperature is about 50° C. lower than that of most other alloys. Work to be referred to later suggests that with a number of other alloys the recrystallization temperature of critically strained extrusions lies very near to the solution-treatment temperatures necessary for the attainment of the full mechanical properties.

VIII.—OTHER METHODS OF CONTROLLING GRAIN GROWTH.

Various investigators in Germany during the war reported attempts to overcome the development of large grain in extruded products which involved making apertures in the die additional to those of the par-

ticular shape required, and so relieving the strain in critical parts of the metal during its flow in extrusion. These efforts do not appear to have been particularly successful, and in any case are not likely to be economically feasible.

The position at the present time, therefore, is that control of the structure of extruded products may best be exercised by a careful study of the characteristics of the alloy being extruded, of the size and shape of the extruded section, of the diameter and length of the billet to be used, and by close regulation of the temperature and speed of extrusion. Factors bearing on temperature consist not only of the temperature of the billet itself, but also of that of the container, the die assembly, and die; and the temperature of the follower plate can have a disconcerting effect on the subsequent behaviour of the extruded section in heat-treatment. In addition, the function of elements which raise the recrystallization temperature of the alloy is an important factor.

There are, however, limitations to what may be achieved in the use of elements of the latter type. It can be demonstrated, in the case of alloys of the Duralumin type, that a considerable increase in the manganese content will enable a very high standard of fine-grained heat-treated extruded sections to be obtained, but in a large majority of cases the mechanical properties of such alloys show deficiencies in certain directions, such as lack of ductility or lack of forgeability, which may preclude their use in engineering applications. In a similar manner the use of undue amounts of manganese and chromium in the aluminium-zinc-magnesium alloys reduces ductility, interferes with the processes of diffusion, reduces the transverse properties, and introduces into the alloys voluminous compounds which may act as stress raisers under the highly stressed conditions which arise in aeronautical engineering. It is clearly apparent that there is ample scope for very extensive research work in this important field of technology.

It will be of interest to examine other methods which have been applied to prevent grain growth in the outer annulus of extruded products.

Many attempts have been made to modify the nature of the flow of the alloys during extrusion by alteration of the shape of the face of the die in contact with the billet. These have generally taken the form of applying a concave shape, with the idea of streamlining the flow of metal and eliminating the zone at the corner of the container and die face, which takes no part in the flow. In some cases a slight diminution in the volume of the metal critically strained may result, but generally this expedient does not appear to offer any real chance of effecting a cure.

It has further been suggested that exaggerated grain growth might

be prevented by subjecting the extrusion to a controlled amount of cold work before heat-treatment. The alloys are very sensitive to these effects, and comment on this suggestion may perhaps be limited to a consideration of what occurs when extruded sections are stamped with metal stamps before heat-treatment. If the extrusions have fully recrystallized before heat-treatment, local areas consisting of large grains will be formed in areas adjacent to the stamp marks during subsequent solution-treatment, while the remainder of the annulus remains of fine grain. If the extrusions have not recrystallized, the reverse effect occurs, and local fine-grained areas adjacent to the stamp marks occur in a field of large-grained material. Experiments have been conducted in which reeling, stretching, and even drawing have been applied to heat-treatable extruded products with a view to eliminating exaggerated grain growth. As will be realized, these operations may in some cases be successful in their object; in other cases large grain has been developed in cold-worked heat-treated products which, in the absence of cold work, would have retained a fine grain on heat-treatment.

Further experiments have been carried out which have aimed at the removal of cold work from the extruded product by heating it to a temperature lower than the solution-treatment temperature before heat-treatment. It was hoped that by this means recovery would occur, and that the strain energy necessary for grain growth would be removed. The experiment recorded here shows that this effect may actually be achieved, but it also shows that what might be called the "recrystallization factor" is so variable that such a method is not a practical commercial proposition. The experiments, however, are of considerable interest, as they furnish useful information as to the condition of the alloys when in the as-extruded condition.

For the purposes of the experiment three extruded hexagon rods in an alloy conforming to specification D.T.D. 423B, which were known to develop a large-grained annulus on solution-treatment at 525° C., were selected. Sample pieces in the as-extruded condition, of $\frac{3}{4}$ in. length, were parted off, heavily pickled to remove the effect of machining, and solution-treated in a salt bath at 525°, 515°, and 505° C., respectively, for 30 min. All specimens were recrystallized to large grain after heating at 525° and 515° C., but at 505° C. only one specimen was recrystallized. Further specimens from each rod were then heated at various lower temperatures, and it was finally established that a suitable temperature lay somewhere in the range 455°–465° C.

Samples from each rod were subsequently annealed for 24 hr. at 465° and 455° C., respectively, air cooled, reheated for 30 min. at 520° C.

and quenched in water. Examination of these specimens showed the interesting results given in Table V.

TABLE V.—*Recrystallization of Extruded D.T.D. 423B Alloy.*

Rod	Annealing Temp. : 465° C.	Rod	Annealing Temp. : 455° C.
XF	Recrystallized to large equiaxed grains.	XG	Recrystallized to smaller, more elongated grains.
YF	Recrystallized.	YG	Recrystallized. One very large grain.
ZF	Recrystallized only near sawn edges.	ZG	Recrystallized, except innermost zone. Elongated crystals.

The annealing was successful in only one case, that of Rod Z at 465° C. Here the outer worked zone was unrecrystallized except for a few very elongated crystals which had started from the sawn edge and were isolated from one another. For the main purpose of the experiment they may be ignored, but they showed clearly that crystal propagation is much easier along the extruded section than across it. Heating at 455° C. for 24 hr. was evidently not sufficient to prevent recrystallization.

Rod Y was not of particular interest, but Rod X illustrated the dependence of grain-size on the number of nuclei; at 465° C. nuclei were nearly removed, and the grain-size was large; at 455° C. the grains were more numerous and smaller.

The experiment showed that in one case only did a preliminary anneal prevent recrystallization on heat-treating an extruded section at 520° C., and this was at a temperature only 10° C. lower than that of a treatment which produced recrystallization of itself. An anneal 10° C. below the successful one was not adequate. On the other two bars no successful treatment was found. With this alloy the critical annealing-temperature range would seem to be quite small and to vary from bar to bar. Although with other alloys the temperature range might be wider, the process appears to be too critical for any practical application.

Further work was subsequently carried out in which the factor of time at temperature was investigated, but this resulted in no practical information being obtained and is hardly relevant to the general discussion.

One further variable which may affect the behaviour of extruded sections on heat-treatment has been mentioned earlier, namely, heterogeneity of composition. In casting alloys having wide solidification ranges into the larger sizes of billet for extrusion, local variations in composition in the same billet will occur, owing to the natural processes

of solidification, even with material cast by the semi-continuous process. It is considered that these variations will in themselves be significant factors, and responsible for cases in which local grain growth may arise owing to parts of the extruded section being recrystallized under the existing extrusion conditions, while others, of slightly different composition, recrystallize during the heat-treatment operation. In such instances isolated grains of large size may be formed in a matrix of fine grains.

It is perhaps of interest here to refer to difficulties which may be met with in subsequent handling of material that is prone to the development of large grain. One such case is that in which large portions of the extruded section are machined away, leaving in parts of the component thin areas adjacent to the surface which may consist entirely of large grain. Such a condition may occur in the manufacture of aircraft spars of tapering section. With the new high-strength alloys of the aluminium-zinc-magnesium type, effective control of this factor can now be maintained, and the problem is likely to become insignificant; in many cases consultation between the maker and user of an extruded section at an early stage in the design will enable a satisfactory solution to be reached.

A more difficult and vexed problem is that of the use of extruded bar as forging stock, and at the risk of intruding on the subject matter of another paper in this Symposium it is felt that some reference should be made to this. Fig. 8 (Plate LXII) is a photomicrograph of an extruded bar which has been forged at 420° C. to a tapered shape, so producing a variation in the amount of hot work, and subsequently heat-treated. It illustrates the fact that the difficulty of the development of large grain in heat-treated forgings may be overcome by giving the stock sufficient work in forging. In a great number of cases it is not economical or even practicable for the forger to apply large amounts of forging, and when this is so a choice of material should be made either from the front portions of extrusions, or from material which has recrystallized fully in the extrusion process itself.

IX.—QUENCHING AT THE DIE.

Since the product of the extrusion process leaves the die at a temperature which approximates to the solution heat-treatment temperature, attention has naturally been directed to the possibility of achieving solution-treatment of heat-treatable alloys by quenching them as they emerge. The process is quite simple, and has the advantage that the development of large grain in the periphery may be avoided. Quite a large quantity of material is produced in this manner.

Material quenched at the die may, of course, develop large grain if subsequently solution-treated. It is necessary to preheat the billets to a temperature which ensures that under the extrusion conditions obtaining the temperature of the issuing extruded section lies within the solution-treatment range, and to ensure that there is a water spray of a capacity adequate to quench the metal rapidly. In some cases problems may arise when distortion and twisting of complicated sections occurs owing to thermal effects, and great thought has to be given to the method of quenching. Sections up to 2 in. thick may be effectively quenched in this manner.

The mechanical properties of die-quenched sections are entirely satisfactory, being in some cases even higher than those of sections in similar alloys produced by a separate heat-treatment process. It is of interest to note that the die-quenching of aluminium-zinc-magnesium alloys of the heat-treatable type was carried out in Germany during the war as a routine operation on extrusions for use in aircraft, and it was claimed that no failure to achieve specification properties was recorded. Alloys of this type of composition would seem to be very suitable for the application of the die-quenching technique because their optimum solution-treatment temperature (465°C.) lies nearer to the optimum extrusion temperature than it does in the case of other heat-treatable alloys. A further claim by German technicians was that die-quenched extrusions in these alloys were not recrystallized, and that in consequence their resistance to stress-corrosion was higher than that of similar alloys produced by separate heat-treatment. This latter statement is open to some argument, since alloys of this type are not usually recrystallized when normally heat-treated.

X.—THE CHARACTERISTICS OF EXTRUDED PRODUCTS.

When the extrusion of a bar first begins, a slug of cast metal exactly opposite the die orifice is squeezed out, and this slug suffers practically no deformation. Its structure is as cast and its properties are virtually those of cast metal. This portion of the extrusion is usually cut off and discarded, its length being roughly equal to the bar diameter. As extrusion proceeds metal flows in from the back and sides of the die orifice, suffering more and more deformation. Gradually the intensity of the shear forces develops, and when about half of the extrusion is completed metal from the highly worked area begins to influence the structure of the bar, forming a clearly defined annulus of fine grain on its periphery. As extrusion continues the annular area increases in size, and the outer annulus of the extruded bar gradually thickens. If extrusion is carried sufficiently far, the whole cross-section of the

bar may consist of metal from the heavily worked area. Such a state of affairs is not allowed to happen in practice, since at this stage the more freely flowing metal at the centre of the billet has passed through the die and metal is drawn in from the sides and rear end of the billet so that the centre of the bar becomes hollow, giving rise to the "extrusion defect". In order to prevent this condition arising, extrusion is discontinued when 10–15% of the billet still remains in the container.

Many misguided attempts have been made to prevent the formation of the extrusion defect by varying the shape of the follower plate, by roughening its surface in contact with the back end of the billet, or by cutting grooves in its surface. Such expedients, if carried too far, may actually aggravate the defect by inducing shear cracks in the alloy at a stage in the extrusion process prior to the formation of pipe. When a method of preventing the extrusion defect is found, its application will lie in facilitating flow at the front end of the billet, and not in hindering it at the back end.

An extruded product, therefore, is not uniform in its structure from front to back. At its front end the structure is substantially as cast; at its back end the structure is well wrought. The structure at the middle of the length of the extruded bar is intermediate between these two. Fig. 9 (Plate LXIII) shows the microstructures of a 2-in.-dia. Duralumin bar (*a*) 1 in. from the front end, (*b*) 1 ft. from the front end, (*c*) at its middle, and (*d*) at its back end. The specimens illustrated are of surfaces parallel to the main axis of the bar, and they show clearly the marked way in which the metal is elongated. Both the grains of the matrix and the clusters of compounds in the alloy have been considerably drawn out in the longitudinal direction. The effects of these characteristics on the mechanical properties of the extruded product are not so marked as may be imagined, and vary somewhat from one type of alloy to another. Typical properties for three different alloys are shown in Table VI.

TABLE VI.—*Typical Tensile Properties of Aluminium Alloy Extrusions.*

Alloy	Position	0·1% Proof Stress, tons/in. ²	U.T.S., tons/in. ²	Elongation, % on 2 in.
B.S. 6L1	Front	18·5	30·5	18·0
	Back	20·2	32·0	15·0
D.T.D. 364B	Front	27·5	33·5	12·0
	Back	28·4	34·0	10·0
B.S./STA7/AW6	Front	8·2	17·4	25·0
	Back	8·5	17·8	23·5

The figures given were obtained from test-pieces taken in the longitudinal direction. Alloys which contain large quantities of insoluble alloying elements, however, have much lower mechanical properties when tested in a transverse direction. In relation to transverse properties, therefore, the composition of the alloy, the method of casting, the size of the extrusion billet, and the cross-sectional area of the extruded section itself, are of considerable importance.

XI.—EFFECT OF REDUCTION OF AREA ON CHARACTERISTICS OF EXTRUDED SECTIONS.

Observations have already been made on the lower mechanical properties which are normally obtained on heat-treated extruded sections of less than $\frac{3}{8}$ in. thickness. In such cases the ratio of the area of the extruded section to that of the billet from which it is extruded is very low, and the sections are more highly deformed than sections in which the ratio of reduction is higher. In consequence, the insoluble constituents, which normally interfere with the processes of crystallization, become finely broken up, and are not laminar as in the larger extruded sections, so that crystals are usually more equi-axed in the smaller ones. There is, therefore, some evidence that with many of the heat-treatable alloys too low a ratio of reduction will lead to lower mechanical properties. For the most satisfactory mechanical properties with the Duralumin-type alloys a ratio of 1:15 is admirable, and properties remain reasonably consistent down to a ratio of 1:8. Beyond this, the structure becomes insufficiently wrought, and as a consequence the ultimate tensile strength and in particular the elongation naturally fall. The effect of reduction of area varies with the characteristics of the alloy being extruded, and in the case of some of the non-heat-treatable alloys, where the mechanical properties of the alloy in the cast condition more nearly approach those in the wrought condition, a wider ratio of reduction may be successfully applied. Usually the limiting factors are that the section, if too small, does not permit of extrusion, while if it is too large the sheared area of the billet being extruded becomes very local and the shear stresses fracture the metal during extrusion, causing the formation of large blisters or double skin on the outer surfaces. In the case of very small extrusions the difficulty referred to above is, of course, relieved by the use of multi-hole dies.

XII.—MULTI-HOLE DIES.

It is obviously an attractive economic proposition to extrude through multi-hole dies, and in a great many cases the product of the

multi-hole die will give entirely satisfactory properties. In those alloys that are prone to segregation, and particularly in the case of very large-diameter billets, where the structure at the centre may be coarse, care should be exercised in using multi-hole dies. In such cases it is better to choose a smaller billet diameter and extrude through a single-hole die. Northcott⁷ and his co-workers have dealt adequately with this difficulty, and have indicated that the placing of a hole in the centre of a multi-hole die is a good palliative.

With the heat-treated alloys the use of multi-hole dies may result in the formation of structures which are undesirable owing to the fact that the annular area of large grain may be distributed between the various rods extruded simultaneously, giving a crescent-like effect to the macrostructure. Where extruded bars of this type are made from billets having a coarsely segregated central structure, the bars will frequently crack on quenching along a line corresponding with the part of the periphery of the bar which was aligned with the centre of the cast billet.

XIII.—EXTRUSION OF TUBES.

It is not proposed to deal in any detail with the extrusion of seamless tubes. Most of the problems which arise are engineering problems, the metallurgical factors being in general the same as in solid extrusion. Where mandrels of the normal type are used in conjunction with hollow billets it is difficult to produce hollow extruded tubes which are entirely concentric, and it is the normal practice to extrude blooms of relatively large size, reducing them to finished size by a variety of cold-working operations.

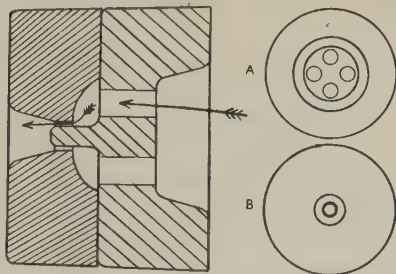


FIG. 11.—Diagram of Ante-Chamber Die.
A. Back view. B. Front view.

It is, however, of interest to refer to an alternative method of making tubes and hollow sections of small sizes and precise dimensions, namely by the use of ante-chamber or bridge dies. In this application of the extrusion process the principle of pressure- or recrystallization-welding is involved, and the hollow shapes are produced from solid, i.e. unbored, billets. One type of die is illustrated in Fig. 11.

It will be seen that the process consists of extruding a number of solid rods simultaneously into an ante-chamber, in which they are

subjected to pressure and marked deformation as they pass into the annulus between the mandrel and the extrusion die. It is important that both the tools and the alloy billets be kept scrupulously clean, and that the temperature and speed of extrusion be kept within specified limits; otherwise the welds will be imperfect. Provided the process is carried out correctly, the products have a strength and soundness equal to those of tubes produced by the mandrel process; indeed, it is often difficult, even on a polished and etched cross-section, to detect the areas where welding has occurred. Tube produced by this process may be drawn down cold quite successfully, to smaller sizes.

The process has its limitations, however. The stronger alloys have not been produced economically by this method, as dies have not yet been designed which will stand up to the work. Even with the softer alloys pressures are high, and with alloys of the Mg_2Si type extruded at very high temperatures, pressures on the die may exceed 60 tons/in.²

XIV.—NON-METALLURGICAL FACTORS IN EXTRUSION.

An attempt has been made in this discussion of extrusion to concentrate on the features of the process that are related to hot working, and the engineering aspects of the process have been only lightly touched upon. Certain troubles may arise in the production of extrusions which can be described as non-metallurgical, and these will be discussed briefly in order to give some degree of completeness to the paper.

The first instinct of the operator of the extrusion press is to use some kind of "lubricant" to prevent the aluminium alloy from adhering to his tools. A popular lubricant of this type is graphite or a mixture of oil and graphite. Such lubricants should be avoided as far as possible, for if they are used too liberally they will penetrate the billet and emerge just below the surface of the extruded section, giving rise to non-metallic inclusions and blisters.

A factor which may cause blistering of extruded sections is that of container wear. The liners of extrusion containers are subjected to considerable abrasion and they gradually assume a barrel-like shape. When this happens the residue will adhere to the surface of the next billet being extruded, and when it reaches a critical thickness it will penetrate the billet and be drawn into the extruded section, giving rise to oxide stringers and surfaces of separation just below the surface of the extruded section.

It is important to maintain the ram of the extrusion press in good alignment with the container. A ram which makes contact with the shell of metal adhering to the container wall will cause blistered surfaces

on the extruded section in line with the portion of the ram in contact with the container.

The surface quality of the billet being extruded should be good. It is true that a thin layer of metal adjacent to the container wall is sheared from the billet in the extrusion operation, but surface billet defects of quite small proportions may be drawn into the extrusion and become concentrated just beneath the surface of the section. This type of occurrence is illustrated in Fig. 10 (Plate LXIV). The billet illustrated had developed cold shuts in casting. The billet was machined down until the deepest cold shut was $\frac{1}{2}$ in. below the machined surface. The extruded discard illustrated shows how these shuts have been drawn together as the billet became shorter during extrusion, and indicates that a fairly good quality of billet surface is necessary.

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THE HOT FORGING AND HOT STAMPING 1227 OF ALUMINIUM AND ITS ALLOYS.*

By F. E. STOKELD,† F.I.M., MEMBER.

SYNOPSIS.

The general aspects of forging aluminium and aluminium-rich alloys are reviewed, and some of the essential differences in practice between the forging of these materials and the forging of steels are indicated. The difficulties associated with the accurate estimation of the values of strength and ductility ruling at particular locations in forgings of the aluminium alloys are already well known, but the aircraft industry, especially, requires assurances of minimum values at various locations in important forgings. This problem is discussed, together with the influence of various factors which have a bearing upon it, such as the alloy used, the forging stock, its size, method of manufacture, the methods and temperatures employed during the forging and subsequent heat-treatment operations, and the final shape and flow lines produced in the various parts of the forging itself, &c. Frequent reference is made to published work.

I.—INTRODUCTION.

Up to the early 1920's very little was heard of forgings in aluminium and the few aluminium alloys then available. Duralumin and Y alloy were beginning to appear in the form of forgings, and one of the earliest published accounts of some of the practical aspects of the manufacture of these forgings in dies was given by Whiteley¹ in 1925. This paper indicated that Duralumin does not flow as readily as steel and that proper heating of the stock is very important; that in the design of forgings and dies, all sharp corners are to be avoided; that die surfaces must be very smooth; that light blows of the hammer should be used, especially at the commencement of forging roughly to shape, but that when the properly shaped piece is being forged in the closed dies "... the full weight of the hammer must be employed so as to completely fill the impression in the finishing dies". These are, of course, some of the basic necessities of aluminium alloy forging; that they were realized 25 years ago may be surprising.

In those early days when the alloys were new, their forging characteristics were always compared with those of steel. Indeed, they are still.^{2, 3, 4, 5} A great deal of experience had been gained in the forging

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of steel, but few workers had dealt with the matter on anything like a scientific basis; indeed, forging was more an art than the practice of a controlled metallurgical process.

There existed, of course, the laws of deformation formulated by Tresca as long ago as 1867 and 1878.⁶ These have been discussed more recently by Southwell⁷ in 1941, and Chartron⁸ uses them, particularly as applied to the upsetting of a billet, and shows curves for Duralumin.

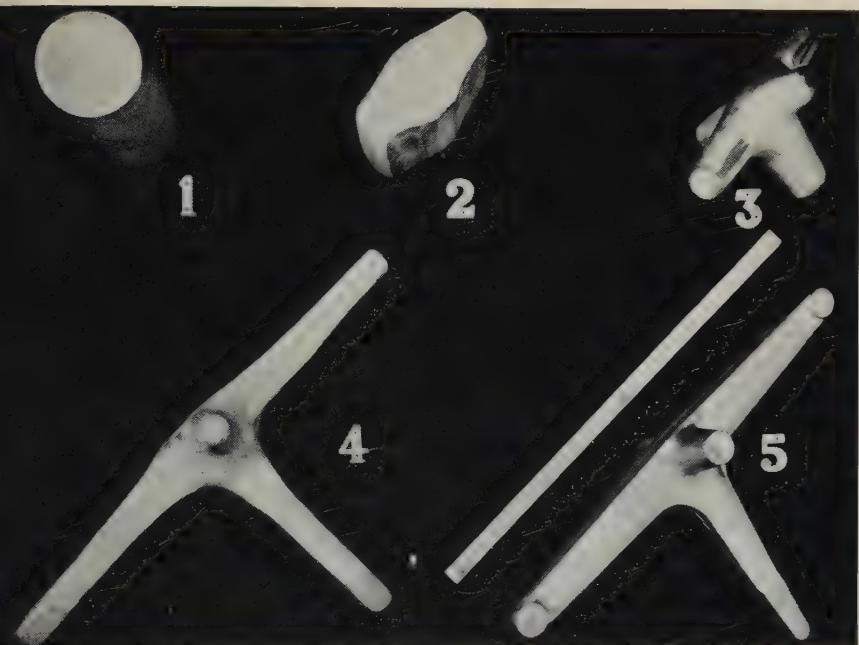
Massey³ in 1923 presented the results of his study of the effects of hammer- and press-forging when using plain pallets, by means of models in wax and other materials.

In 1931 Devereux⁹ discussed the mechanical properties of some of the strong aluminium alloys in the cast, extruded, and forged conditions, followed by final heat-treatment, and the effect of reheating temperature upon their tensile properties and hardness. He also drew attention to certain characteristics of cast and extruded stock which can give rise to various defects in forgings made therefrom.

After those early days, little fundamental work was published recording the properties which result from the fabrication of aluminium alloy articles by forging, though Sachs¹⁰ discussed the matter in detail in 1939. More recently, a number of other publications have appeared on the forging of aluminium alloys, and a selection of these is listed among the references.¹¹⁻¹⁴ A very comprehensive work¹⁵ on the forging of steel gives full details of plant and equipment used, methods of production, dies, die and tool steels, &c. The essentials of forging practice are so fully covered, whatever the metal to be forged may be, that it is unnecessary in the present paper to discuss such normal requirements. There are, however, certain differences which ought to be taken into account when the forging of aluminium alloys is being considered and some of these will be mentioned briefly.

II.—SPECIAL REQUIREMENTS OF ALUMINIUM ALLOYS.

The energy required to achieve a given deformation is greater for aluminium alloys than for common steels. Alden² states that 30% more power in the hammer, or press, is needed. Other authorities quote varying figures, but all agree that considerably greater force is required because the material flows less readily at the forging temperature than does steel, and it follows that highly polished dies and tools, with proper blending of the different sections and larger radii, are necessary. However, the best modern forging practice for steel and other materials calls for these as essentials in order to ensure the proper flow of the material for the fulfilment of the strength require-



(By courtesy of The Deritend Stamping Co., Ltd.)

FIG. 1.—Billet "Uses" and "Dummies" for Making Three-Arm Forging.

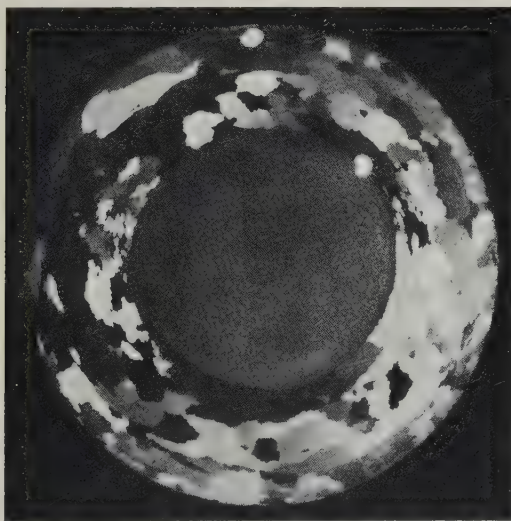
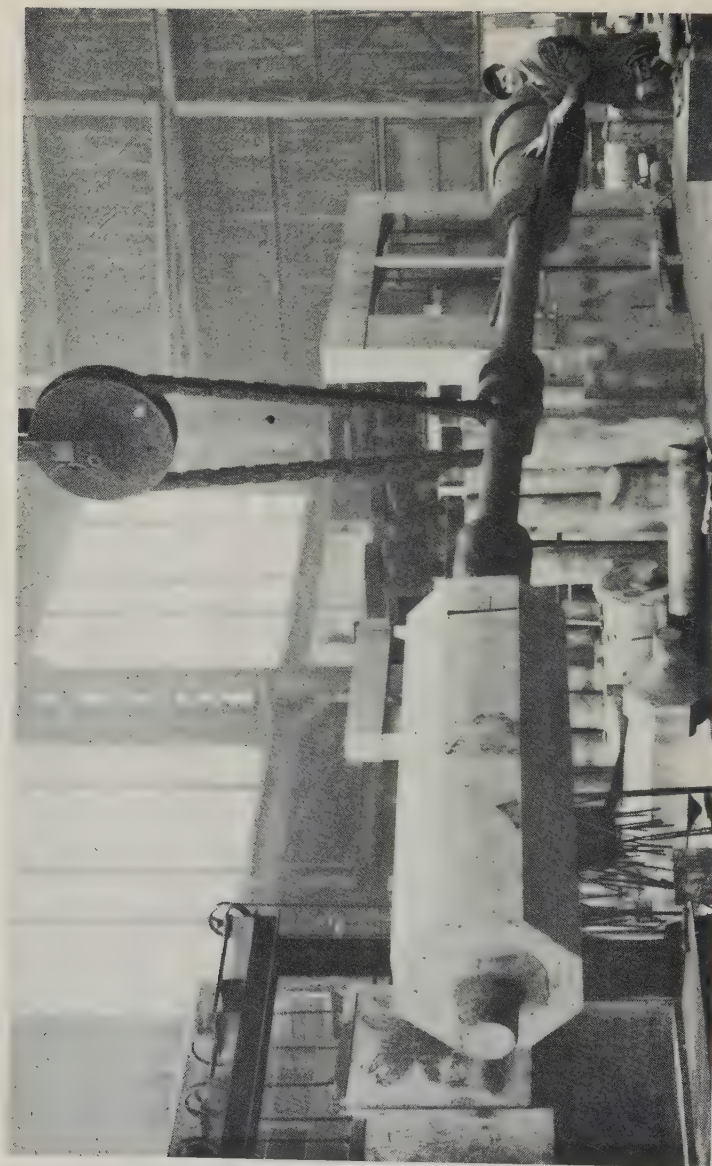


FIG. 2.—Excessively Coarse Grain in Extruded Stock.

[To face p. 454.]



(By courtesy of Messrs. James Booth and Co., Ltd.)

FIG. 3.—30-in. Octagonal Billet for Forging.

ments of the forging. Furthermore, some of the more recent heat-resisting ferrous alloys possess even less capacity for plastic flow than the aluminium alloys.

Pure aluminium is seldom used for the production of modern forgings. It has a very low strength after forging hot, but it may be forged at lower temperatures. Even when forged cold, the strength attained is hardly sufficient to warrant the expenditure of time and power. Char-
tron⁸ quotes an example of both the hot and cold forging of pure aluminium centrifuge bowls and gives the mechanical properties obtained thereon. The elastic limit was raised from 7 to 10 kg./mm.², the U.T.S. from 9 to 12 kg./mm.², and the elongation was reduced from 18 to 5% by forging cold instead of hot.

TABLE I.—*Composition and Forging Temperature of Aluminium Forging Alloys.*

No.	Type	Relevant Specification *	Approximate or Typical Composition						Forging Range, ° C.
			Cu, %	Mg, %	Si, %	Fe, %	Mn, %	Other Elements, %	
1	Al-Mg	STA7-AW6A (MG5)	...	5.0	...	0.4	0.5	...	400-320
2	"	NF7 (MG7)	...	7.0	...	0.4	0.5	...	400-320
3	Al-Mg-Si	HF10 (51S)	...	1.0	1.0	0.5	0.7	...	450-360
4	Al-Si	D.T.D. 324 (32S, LO-EX)	0.8	1.0	11.5	Ni 1.0	430-360
5	Al-Cu	HF17, L25 (Y Alloy)	4.0	1.5	Ni 2.0	450-360
6	"	L42 (R.R. 58)	2.2	1.5	...	1.2	...	Ni 1.0	450-360
7	"	HF14, L1, L39, D.T.D. 150 (Duralumin)	4.2	0.7	0.8	0.5	0.6	...	450-380
8	"	HF15, D.T.D. 364, L45 (Super-Duralumin)	4.4	0.7	0.8	0.9	0.8	...	450-380
9	"	HF12, L40, D.T.D. 130, D.T.D. 184 (R.R. 56)	2.2	0.8	0.9	0.8	...	Ni 1.0 Ti 0.1	480-380
10	"	D.T.D. 423	0.7	1.0	1.0	0.5	0.7	...	450-380
11	Al-Zn-Mg	D.T.D. 683 (R.R. 77)	0.4	2.6	0.2	0.3	0.25	Zn 5.5 Cr 0.1	420-360

* The NF and HF specifications relate to the new British Standard 1472.

An indication of the range of aluminium alloys currently used for forging (though not a full list) is set out in Table I, together with some of the relevant British Standard and Ministry of Supply Specifications. They may be divided roughly into five groups according to their major alloying constituents. The first group is seldom heat-treated after forging, although an annealing operation may be imposed when considered necessary for the purpose of removing forging stresses.

The alloys of all the other groups are heat-treated in order to improve their mechanical properties and the processes applicable to each alloy are shown in Table II. The mechanical properties to be obtained on 1½-in.-dia. forged test-bars after heat-treatment are also included in

the Table. Where single figures are quoted, these indicate the minimum values specified, but the others indicate typical values.

TABLE II.—*Heat-Treatment and Mechanical Properties of Aluminium Forging Alloys.*

No.	Heat-Treatment		Condition	0.1% Proof Stress, tons/in. ²	U.T.S., tons/in. ²	Elongation, %	Brinell Hardness No.
	Solution Temp., °C.	Precipitation Temp., °C.					
1	As forged	8-11	16-20	8-20	...
2	As forged	9-12	20-23	18-25	...
3	510-530	165-175	S only	7-9	12-14	18-25	45-60
4	525-535	130-160 190-210 *	S and P	15-16	18-22	10-20	75-100
5	490-525	5 days room temp.	S and double P	...	20-25	3-8	...
6	520-530	150-170	S and aged	14-17	24-27	15-20	100-130
7	520-530	150-170	S and P	18-20	25-30	6-20	(a)
8	490-500	5 days room temp.	S and P	20-22	27-30	10-16	(b)
9	500-510	5 days room temp. or 175-180	S and aged	15-17	25-28	15-25	100-120
10	525-535	175-180	S and P	14-18	25-28	15-25	100-120
11	510-530	175-180	S and P	26-28	30-33	8-12	130-150
12	455-465	130-140	S and P	21-23	27-30	10-15	120-140
13	455-465	130-140	S and P	20-22	25-28	10-20	110-130
14	455-465	130-140	S and P	27-32	32-35	10	140-165

(a) Piston. (b) Forged bar. * After rough machining. S = Solution-treated. P = Precipitation-treated.

III.—FORGING PLANT.

Whilst the plant required for the forging of aluminium alloys is not greatly different from that used for forging steel, it must be very robust and capable of working accurately. The modern trend has been to increase the size and weight of hammers and presses so as to accommodate and permit of the production of larger and more complex forgings than had been previously used.^{16, 20}

1. Presses and Hammers.

The action of the press is to squeeze the metal, without impact, and deform it quickly in a few seconds; whereas hammers apply pressure by impact, using successive blows, when the pressure is relieved before the metal has fully yielded. Thus, a large number of blows may be required under a hammer to produce, in several minutes, a given deformation which may be accomplished in one squeeze in a few seconds in the press. However, whilst upon upsetting under the press, a limit can be reached, owing to insufficient power to produce further metal flow, the hammer can still continue the upsetting, however small the amount, by repeated blows, so long as the metal is still hot enough.

The relative merits of the forging hammer and press and the laws governing hot working are ably discussed by Chartron.⁸

It has been found that hammers are not suitable for the preliminary breakdown of the cast structure of ingots in some of these alloys, because they will not withstand impact blows without cracking. For this reason the modern practice is frequently to work cast ingots first in the hydraulic forging press, down to the desired shape and size (called a "dummy" or "use") and then to transfer to dies in a hammer for the final forging operations, or sometimes to an extrusion press.⁸ By this means, the cast metal is prepared in the press better to withstand, without rupture, the impact of blows under the hammer.

In the forging of aluminium alloys several different types of press are used. The most powerful are the hydraulic presses up to about 15,000 tons; in Germany up to 30,000 tons.⁸

There are also available very powerful mechanical presses: crank presses and friction screw presses. During the war years, a very large quantity of extruded and rolled bar was used on the many different sizes of these presses to produce an immense variety of small and medium-sized, accurately finished forgings in great numbers. Some of these presses are also used for trimming the "flash" off forgings, either hot or cold. The upsetting machine may be classed with the mechanical presses and is used for the production of small to medium forgings, as well as to form the hub-flange of propellers.¹⁷

Hammers are designated according to the means adopted for lifting the tup, and their size or power by the weight of the tup which falls, whether the fall is assisted or not. There are steam, pneumatic, and board hammers, as well as the ordinary drop hammer where the tup is lifted by a flexible belt, &c., over a pulley. Some hammers have been produced with tup weights up to 120 tons, but such very heavy hammers are not now used for the purpose of forging aluminium alloys as was originally intended.⁸

2. Dies.

The flow of hot metal under the hammer or press is controlled by the action of the dies which are fitted to the forging hammer or press itself. Dies may be either "open" or "closed".

Open dies have two plane surfaces between which different parts of the piece being forged are progressively worked to make a "hand forging", i.e. one produced approximately to the final shape desired. The hand forging usually requires to be finished by machining, but many are made as "uses" or "dummies" which are further forged in closed dies, so that they are still nearer to the final shape and size desired.

With these open dies, certain smiths' tools such as swages, &c., may be employed to assist in the production of the shape desired, with the flow-line structure properly developed for the purpose intended.

Closed dies are used in pairs, one fitted to the tup and the other to the anvil of the press or hammer. In some presses and upsetting machines, more than one pair of such dies may be employed, so as properly to enclose the stock and finally permit the withdrawal of forgings which have undercut protuberances of one kind or another. In closed dies, all the surfaces of the hot metal are worked at once and, being accurately finished to the desired shape and dimensions, they allow of the production of larger quantities of forgings, having the same form and size, than could possibly be effected by the use of open dies. Since there is virtually no scale on the surface of the forgings, the accuracy achieved is so good that many machining operations may be omitted.

The surface of the impressions cut in the dies and, indeed, all the surfaces in contact with the hot metal being forged, must have generous radii at all changes of section and a smooth, well-polished finish. This is essential to prevent sticking or puckering and to allow the metal to flow as easily as possible whilst being forged.

Before dies are used in the hammer or press, they should be preheated up to 250° C., or higher if possible, in order to avoid unnecessary cooling of the stock, as well as to increase die life. Pre-heating is especially necessary in the case of hot die steel, if "clinking" in service is to be avoided.

The production of blistered forgings made from sound stock can be caused by improper lubrication of dies, as well as by the use of dies of incorrect design, or those having surfaces not sufficiently well polished.¹⁹ Lubrication of the die surfaces is a further means of facilitating metal flow in the piece being forged.^{20, 21} It is effected by a variety of media at different works. The more recent tendency, however, is to reduce the use of die lubricants to a minimum and rely more upon good die design with a highly polished surface finish.

The imposition of a stress-relieving operation by heating dies to near the original tempering temperature after periods of use, has been known appreciably to increase their life.

When using pairs of closed dies, the hot metal in excess of that required to fill the impression is forced out between the dies in the form of a "flash", which has to be trimmed off. The form which the flash line should take and the space to be left between the dies for its accommodation has been discussed by several authors, notably by Sachs¹⁰ and Chartron.⁸ This flash cools quickly and tends to prevent more

metal escaping from the recessed portion of the die than is required properly to fill the impression. Insufficient attention to the correct use, accommodation, and disposal of the flash can lead to much difficulty and many defective forgings. It may be removed at intermediate stages in the production of a forging to permit a further quantity of metal to escape from the impression in the dies and it has to be removed finally. This may be done hot or cold, but usually, trimming carried out cold is best.

The closed dies themselves may contain more than one pair of impressions, for the purpose of successively shaping the hot metal and the flow lines produced therein to the form required for the final impression.¹⁹ Alternatively, the preforming operations may be carried out in separate dies which have been specially cut so as to gather, draw out, and reduce the section or bend it, to form a suitable "use" for introduction to the accurately finished final impression. Sometimes, these preforming operations involve the employment of first, a hand forging, then a pair of "use"-making dies (more than one pair have been used on occasion), next a further hand forging is made from the "use", by which time the stock is deemed to have been sufficiently worked and the flow lines properly disposed in the required shape, and the forging is then ready for finishing in the final pair of closed dies.

An example of such a forging procedure is illustrated in Fig. 1 (Plate LXV), where a $4\frac{1}{2}$ -in.-dia. billet of extruded bar was hot worked to make the forging, which has three arms, each about 12 in. long, around a central boss of nearly 2 in. dia. and $6\frac{1}{2}$ in. in length. All the five different stages of production are depicted in the same relation to one another and with the axis of the original billet always in the same plane. Thus, the direction of the flow lines in the original billet has been maintained in the central boss itself, whilst the three arms were forged out almost at right angles to the original grain flow. The material was ordinary Duralumin and, after the forging had been heat-treated and naturally aged, almost equal mechanical test results were obtained, with good elongation values, on samples which were cut from each of the three arms.

IV.—FORGING STOCK.

Whatever forging technique is to be employed, it is equally true that whilst poor forgings can be made from good stock, good forgings cannot be made from bad stock. Thus, it is essential that suitable stock should be chosen for the particular purpose in mind and that inspection should be carried out to ensure that an adequate standard of quality is maintained in the material, which must be sufficiently free

from defects, or the effects of a preliminary process, to ensure that the forgings produced are not themselves defective on account of the shortcomings of the stock from which they were made.⁹

Recommendations regarding choice of alloy and preparation of forging stock have been published by several authors,^{10, 20, 22, 23} and before proceeding to discuss the matter, it may be useful to consider the varieties of forging stock available, some of their peculiarities, and the defects to which they are liable. There are two main varieties: cast and wrought. These may be subdivided according to their method of manufacture, as follows:

1. *Cast Stock.*

This consists of ingots or billets, depending upon size, made (a) by casting in sand moulds, (b) by casting in chilled moulds, and (c) by the continuous-casting process. Ingots or billets are usually of cylindrical form and have their exterior surfaces cleaned off by machining before use for forging, but very heavy ingots recently produced by a semi-continuous-casting process have been cast in the form of an octagon, ready for forging.

A 2-ton ingot is shown in Fig. 3 (Plate LXVI) and some extruded billets up to 13 in. in dia. are visible in the background. Together, these represent some of the most recent advances in the production of stock for the largest forgings.

Whichever form of forging stock is employed, it should have commenced originally as a good, sound casting, free from porosity, blow-holes, and similar defects. It should be of fine and uniform crystal grain-size with good, fine particle distribution throughout and free from undue segregation. For this reason, chill castings are preferred, or better still, chill-cast billets produced by the continuous-casting process carried out under properly controlled conditions.^{16, 22, 24}

This produces ingots much finer in grain-size than those obtainable in similar mass by the other methods and such ingots more closely approach the ideal casting, i.e. free from dross, shrinkage, gas cavities, structurally and chemically homogeneous; they are also almost completely free from piping defects.¹⁸ Such material possesses important characteristics in its capacity to withstand the severe and intricate forging operations necessary for development of the highest properties in the final forging. Very large and well-worked forgings can be made from this type of stock—larger than from extruded sections whose size is limited by the existing capacity of extrusion presses. The continuous casting process thus represents a very great advance in the metallurgy of aluminium alloys, particularly as it affects subsequent hot-working

processes and permits the employment of a still larger unit-mass of sound metal.

Inspection is necessary to ensure the use of suitable castings, and it is the practice of some forgers to “. . . cut and examine the ingot for each forging over 10 lb. in weight”.⁹

Preheating is carried out under carefully controlled conditions and the ingots are thoroughly soaked at suitable temperatures according to the alloy being used, so as to remove cored cast structures and dissolve and disperse certain constituents, or to do both. The duration of the soaking period is important. The forging operations may be begun directly thereafter.^{2,9}

Further, the proper size of casting must be chosen to produce a particular size of forging.²²

Large castings often contain some of the alloying elements in particles of considerable size which renders their dispersion difficult, and their effect is harmful in the succeeding processes.¹⁰ The breaking up of these particles has been studied during rolling practice,²⁶ thus suggesting what can occur upon forging.²⁵ Impurities can play a part in altering the forgeability of the material,²⁸ and this is a further matter requiring attention, although it has not been the author's experience in industry to encounter serious difficulties due to this cause.

Sound cast stock possesses practically no directional properties; they are produced in it by the subsequent hot-working process.

2. *Wrought Stock.*

Wrought stock is of four kinds :

- (a) Press or hammer forged, or both.
- (b) Rolled stock produced directly from cast ingots.
- (c) Rolled stock produced from extruded billets.
- (d) Extruded stock produced directly from cast ingots.

(a) *Press or Hammer-Forged Stock.*—Most of this type of stock is first forged in a hydraulic press in several directions, in order to break down the cast structure and prepare it for the more severe working under the hammer. After the first or second heating during the early pressing operations, only sufficient soaking time is necessary to bring the mass up to the required temperature again. Following its reduction to about 50% of the original section, hammer forging is begun and if the piece has been worked to the desired shape, stamping operations in dies can follow at once with advantage.

Directional properties are induced in the material by these different processes, when the metal is so worked that the flow lines are properly

disposed to enable the finished forging successfully to withstand the stresses of service conditions.

(b) *Rolled Stock Produced Directly from Cast Ingots.*—There has not, so far, been a large quantity of forging stock made by rolling directly from the cast ingot in this country, but in the U.S.A. most of the medium and small forgings were produced from rolled stock before and during the war years, until sufficient extrusion-press capacity became available.

Directional properties are marked in this kind of material, just as they are in other rolled metals and alloys. For present-day requirements, the existing flow lines may be used with advantage in the production of certain types of forgings, whereas, for others, they must be bent around or dispersed, so as to reduce their adverse effect upon transverse properties where these are of prime importance.

The main advantages of this type of stock are that it already possesses a well-defined, wrought structure and is much less liable to such variations of grain-size as can occur in extruded stock, or in forging stock which is rolled from extruded billets. It can be produced in a variety of sections and sizes to suit many different applications. Inspection for defects such as laps, seams, and other surface flaws, or possibly unsound centre (if early breakdown was too heavy), is necessary. Internal soundness and cleanliness greatly depend upon the virtues of the original casting process employed, as well as upon the size of the original ingot in relation to the size of rolled section produced therefrom.

(c) *Rolled Stock Produced from Extruded Billets.*—This type is somewhat similar to (b) in character, but it can suffer from practically all the defects of the two types of forging stock (b) and (d), to which it is related, especially when the original billet surface has not been removed by machining to a sufficient depth (scalping) before rolling.

(d) *Extruded Stock Produced Directly from Cast Ingots.*—By far the greatest tonnage of aluminium alloy forgings produced in this country during the war years was made from the directly extruded type of forging stock. Extruded bar can be obtained in the largest variety of sizes and sections, up to about 13 in. dia., and possesses an extremely well-worked, dense structure. When produced by the best methods and having no marked tendency to develop areas of excessively large grain-size, it makes excellent forging stock, provided that its marked directional properties can be used or overcome, when they are important in the final forged product.

Inspection is necessary to ensure freedom from surface imperfections, interior unsoundness, to ascertain that adequate discards have been

made and that significant areas of large grain-size are not developed upon simple solution-treatment. A bad example of coarse grain development in extruded stock by heating to solution-treatment temperature only is illustrated in Fig. 2 (Plate LXV).

Crystal size in extruded stock is a matter of prime importance.¹⁸ Especially is this the case when the manufacture of solid, cylindrical forgings is being considered, whose interior is bored out, leaving only a thin wall with various protuberances, such as attachment bosses, forged upon it.

When forgings contain significant areas of very coarse grain-size of this kind they are rendered weaker thereby. Fig. 4 illustrates the type of load-elongation diagram produced when testing both the interior material of fine grain-size and that of very coarse grain-size found on the exterior of the same extruded bar after being forged at normal temperatures and fully heat-treated.

Evidence of the existence of this very coarse-grained material in different aluminium alloys has been mentioned briefly by several authors, e.g. Devereux^{9,29} and Handforth and Towns Robinson.¹⁸ Fortunately, however, the amount of extruded forging bar with a tendency to include significant areas of very coarse grain-size has considerably decreased during recent years in this country and also in the U.S.A., where similar difficulties were encountered during the war years.

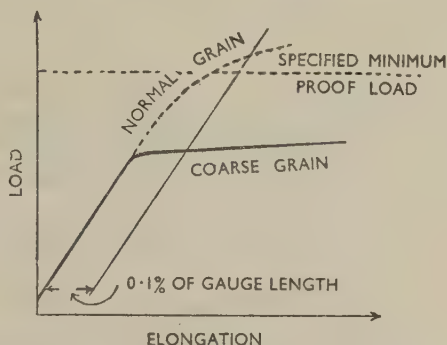


FIG. 4.—Effect of Very Coarse Grain on Load-Elongation Curve.

V.—HEATING FOR FORGING.

The type of equipment used to preheat forging stock is too well known to warrant description here and the usual ranges of forging temperatures have already been given (see Table I). Several authors have published work on this very important subject of heating for forging, coupled with that of forgeability, e.g. Davies²⁰ and Bastien,²⁷ whilst others have studied the transfer and loss of heat during the actual forging operations.^{30,31} Very briefly, the conclusion reached is that there are quite definite optimum ranges of temperature in which par-

ticular types of hot working must be carried out, if the highest possible mechanical properties are to be secured in the finished forging.

An example is set out in Table III to indicate some of the differences in mechanical properties which were encountered following the die-forging of the same, very simple shape in three different alloys (cf. Table I, Nos. 7, 8, and 9) at different temperatures. The stock used was extruded bar and only longitudinal test figures after full heat-treatment are quoted.

TABLE III.—*Effect of Forging Temperature on Mechanical Properties of Aluminium Alloys.*

Forging Temp., ° C.	Duralumin			Super-Duralumin			R.R. 56		
	0.1% P.S., tons/in. ²	U.T.S., tons/in. ²	Elongation, %	0.1% P.S., tons/in. ²	U.T.S., tons/in. ²	Elongation, %	0.1% P.S., tons/in. ²	U.T.S., tons/in. ²	Elongation, %
480	14.9	27.0	25	31.0	34.9	8.5	22.5	28.8	12
450	15.0	27.7	27	31.3	34.8	7	22.4	28.9	12
420	13.9	27.5	28	29.3	33.4	8.5 *	22.5	28.6	13
390	13.8	27.4	27	29.1	32.3	2.5 *	22.0	28.7	13

* Flaw in test-piece.

VI.—MECHANICAL PROPERTIES OF FORGINGS.

In discussing the mechanical properties of aluminium alloy forgings it must be remembered that, unlike other manufactured forms in which these alloys are produced, e.g. sheet and extrusions, forgings do not lend themselves readily to the intelligent anticipation of strength and ductility values. Indeed, at the beginning of most of the British Standard Specifications covering forgings in these alloys, attention is drawn to this difficulty: it must not be assumed that the forgings themselves will possess the same tensile strength, &c., as the test-pieces which were heat-treated with them.

It is no easy matter, except perhaps, in instances of continuing quantity production, to lay down values of proof stress, ultimate stress, and elongation for specification purposes. Modern requirements of the aircraft industry, however, call for decisions to be made as to what minimum properties may be expected from test-pieces extracted from fixed locations in the actual forgings.

The problem of intelligently anticipating these properties in new patterns of forgings is one which calls for the closest co-operation between the aircraft industry, the makers of their forgings, and the suppliers of forging stock. The problem is complicated by the variety of sizes and shapes in which strong forgings are demanded. It has its

root in a number of metallurgical factors of marked influence and there remains the fundamental difficulty of deriving satisfactory mathematical formulæ to represent the influence of progressive tri-axial hot working in open dies, followed by local displacement, or redistribution of metal in closed dies. However, by building up a background of knowledge based on the results of numerous tests taken upon samples cut from a great variety of sizes and shapes of forgings in the various alloys, it is being found possible in the forging industry to face the problem more confidently as the work proceeds and new advances are made.

Some of the earlier results were reported in 1935 by Towns Robinson,³² who remarked on the striking uniformity in the results obtained on test-pieces cut from forgings in R.R. 56 alloy. Elongation values

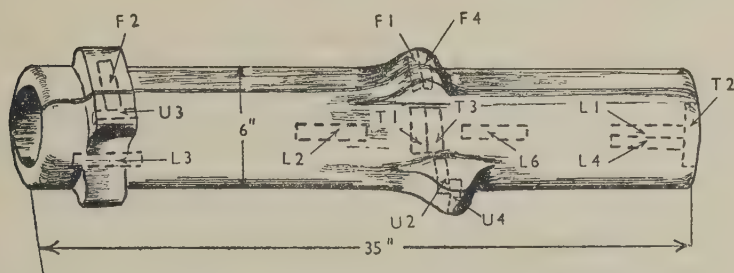


FIG. 5.—Location of Test-Pieces in Long, Cylindrical Forging.

of 10–16% were then reported. Accounts of some recent work on these lines appeared in the U.S.A. in 1944²⁰ and in this country in 1946.³³ There are, however, records of a great many test results on cut-up forgings in the possession of the forging industry in this country and abroad. Some firms have put in hand still more work of this kind, allied to new investigations of forging technique, with a view to improving the strength of forgings and making them still better able to withstand the stresses of arduous service conditions, especially for the aircraft industry.

An example may be quoted here to show how the mechanical test results obtained on forgings are influenced by the direction in which the test is taken.³³ Fig. 5 shows the location of a number of test-pieces in a long, cylindrical forging with various lugs forged upon it. It was produced in closed dies from an 8-in.-dia. extruded bar in the aluminium–zinc–magnesium alloy complying with specification D.T.D. 683. Its weight is given as 15½ lb., but, as depicted, the centre of the original forging appears to have been bored out; otherwise, the weight of the

solid cylinder would have been over 100 lb. Table IV gives the mechanical test results according to the different locations of the test samples.

TABLE IV.—*Mechanical Test Results on Test-Pieces from Cylindrical Forging to Specification D.T.D. 683 (see Fig. 5).*

Direction	Longitudinal				Across Flash		Transverse		Across Lugs			Specification Minima
Test-Piece No.	L1	L2	L3	L6	F1	F2	T1	T2	U2	U3	U4	
0.1% P.S., tons/in. ²	28.9	28.6	31.4	29.8	28.7	29.6	29.4	29.3	29.6	28.6	29.5	27
U.T.S., tons/in. ²	33.3	33.0	34.4	33.6	31.6	33.9	33.1	33.1	33.0	33.0	31.2	32
Elongation, %	18.3	17.5	10.8	12.5	1.7	4.2	7.5	6.7	5.0	17.0	1.0	10
Test-Piece No.	L4				F4		T3	
Izod value, ft.-lb.	4.5; 5.5				1.2		1.4; 1.3	

During the production of this forging, a general reduction in dia. from 8 to 6 in. has evidently been made on the billet, except where the lugs project from the cylindrical surface of the body. There appears to have been comparatively little displacement of flow lines from those in the original bar except at the flash line.

From Table IV, it is apparent that the 0.1% proof stress and the ultimate stress values obtained were very regular on all the samples, whereas the elongation figures showed an irregular scatter. Izod impact values on aluminium alloy forgings are seldom published. Those which have been reported are so low, as compared with the Izod figures regularly obtained on wrought steels, that, in the author's opinion their real value is open to doubt. It is interesting, however, to observe that transverse specimens, whether taken "across the flash line" or not, give considerably lower values than those of longitudinal samples.

The influence of the alloy upon the mechanical properties in the three main directions is discussed by Sachs,¹⁰ who states that "... The mechanical properties of forgings depend chiefly upon two factors: (1) the properties of the original material; (2) the direction and magnitude of the deformation imposed at the point in question".

It is also well known that when only a small amount of deformation takes place at a given point, there is very little difference in the general properties from those of the original forging stock. This holds for many kinds of die forgings, e.g. those which are rather like a plain bar, even those with bosses and protuberances (cf. Fig. 5). But it will be observed how great is the scatter of elongation values in the various

directions, after forging to a comparatively small extent, when the position of the original flow lines is altered somewhat. On the other hand, large amounts of deformation carried out under very high pressures can exert a beneficial effect on the general properties.¹⁰

With these basic principles in mind, forgers have continued to build up their records of day-to-day experience, which is the source of the background knowledge that is so essential if proper progress is to be made and the more modern and stringent requirements are to be successfully fulfilled by forgings in these alloys. Two points have already emerged from a study of some of this background knowledge, and these are found to assist in simplifying the general problem to some extent.

The first is that the general rule appears to hold that proof stress and ultimate stress values are not greatly affected by the disturbing influences (e.g. flow lines, flash line, direction of loading, &c.) in the forging. On the other hand, the elongation value can be much affected. Consequently, there is greater difficulty in correctly anticipating elongation values at specific locations in a forging than in anticipating those of proof and ultimate stress. There are, however, some indications of possible exceptions to this "rule" which should not, therefore, be taken as fully established.

The second point to emerge is that, provided the maximum degree of uniformity of properties for the purpose intended is ensured in the hand forging, or "use", before its presentation to the final impression in closed dies, the subsequent die-forging operations can only be regarded as beneficial. There is one proviso attached to the final die-forging operations, viz. they must be properly designed and performed correctly.

Importance of Elongation Value.

From the point of view of the designer of stressed structures, the elongation value is a very important factor, yet the correct assessment thereof in the forging is the more difficult portion of the general problem to be faced. Thus, it may be asserted that the essential matter for consideration is to trace and attempt to evaluate the influence of the various modifying factors on the resultant elongation values at specific locations in the forging.

Some of these factors may be briefly discussed :

(1) *The Influence of the Original Stock to be Employed, Its Size and Method of Manufacture.*—When undertaking new assignments it is always necessary to determine (from previous case-history if possible) the maximum useful diameter of cast stock for each alloy. Beyond

this point a marked decline in potential strength and ductility may set in, and this is largely dependent upon castability factors of the alloys concerned, as well as the metallurgist's efforts to overcome the difficulties involved.

Devereux,⁹ Sachs,¹⁰ and James²² published earlier work on this matter, whilst Hérenguel²⁴ has recently given an account of his study of continuously-cast ingots and billets for subsequent working.

Recent industrial experience has confirmed that the use of forging stock produced from continuously-cast material will lead to potentially higher strength and elongation values than that produced by one of the older methods. Further, this superiority has become evident over the whole range of sizes and is of particular value in the case of very large forging stock. Complete acceptance of this generality might be somewhat dependent upon the relative freedom from casting difficulties of the various alloys concerned. However, examples from current production in this country serve to indicate the higher standards of excellence, even in larger sizes, which have recently been achieved.

Octagonal ingots of Super-Duralumin alloy (cf. Table I, No. 8) up to 30 in. across flats and about 2 tons in weight, such as that illustrated in Fig. 3 (Plate LXVI) (cf. p. 460) have been successfully cast by the semi-continuous process. These large ingots, as well as large extruded billet stock up to 13 in. in dia., made from cast ingots produced by the semi-continuous process, have been successfully forged on a hydraulic press whose maximum capacity is in the region of 12,000 tons. Some very large forgings with a finished weight of up to 3000 lb. have been produced in this press, and test samples cut therefrom have given very good mechanical properties in different directions.

TABLE V.—*Mechanical Test Results on Test-Pieces from Heavy Press Forgings in D.T.D. 683 Alloy.*

Direction	Longitudinal			Transverse		
	0.1% P.S., tons/in. ²	U.T.S., tons/in. ²	Elongation, %	0.1% P.S., tons/in. ²	U.T.S., tons/in. ²	Elongation, %
Minimum	31.9	35.3	8.0	26.1	31.6	6.5
Maximum	33.2	37.6	12.0	32.5	37.1	11.0

An indication of the level of mechanical properties attained by some press forgings of rather smaller size is given in Table V. This shows the minimum and maximum properties obtained from test-pieces cut out in both directions from nine forgings to specification D.T.D. 683, each of 400–1000 lb. in weight.

(2) *The Influence of the Sequence of Working the Stock.*—For any alloy and size of stock, the maximum working following initial upsetting is that achieved by forging the blank in the remaining two co-ordinate directions, so that the best uniformity of wrought structure is assured. For many sizes this early working may often be applied at one heating only. Again, for many purposes, it may not be really essential that complete tri-axial working should be applied to develop sufficient strength and ductility for the particular purpose in hand.

It must be realized that whilst a shortened forging sequence might be applied successfully to one alloy of low total alloying content and well balanced for casting purposes, the same procedure, if applied to a more highly alloyed material of the same stock size, may lead to failure on account of very low transverse elongation values.

It should be observed with some care that there is a tendency for strength and ductility values to decline in the unfavourable direction, i.e. the short, transverse direction which is the one at right angles to both the principal and secondary axes of working. For example, test samples cut across the minor dimension of a flat, square, or rectangular blank are taken in the unfavourable direction. These samples will exhibit the tendency mentioned, which is found most frequently in the more highly alloyed mixtures.¹⁰ It is considered that the combined influences of grain-boundary orientation, non-metallic inclusions, inter-metallic compound, and residual ingotism largely account for this phenomenon.

(3) *Modifying Influence of the Shape Factor.*—For many hand forgings of a generally flat contour, some slight reductions in strength and ductility may be of relative unimportance, in that high service stresses are not applied in this direction. The same remark might apply to die forgings where reduced properties are exhibited in the direction across the flash line.

Hand forgings are produced roughly in the shape required for machining, or they may be made as “dummies” for forging in dies. There will be an unfavourable direction for elongation value in each of these, but one advantage of forging in closed dies is that it provides for a localized flow of material at chosen points. Die forging can do much to reduce the possible influence of a decline in properties in the unfavourable direction, provided that opportunities are taken at the design stage to enlarge the effective section and/or to improve the metal-flow characteristics, if necessary.

There can be a source of danger, however, in machining lugs on hand forgings, unless there is the assurance of known properties which are adequate and suitable for the design of such offset portions.

VII.—HEAT-TREATMENT.

The main object of heat-treatment is to develop the strength of these alloys to the highest level and so to complete the work of producing forgings which are able successfully to withstand the stresses and strains of service conditions. It is in the achievement of this object by heat-treatment that certain problems arise.

The temperature of the water in which the forgings are quenched from solution-treatment temperature can have a marked influence upon, for example :

- (a) the level of mechanical properties attained;
- (b) the setting up of internal stresses in the forgings.

As a rule, the use of cold water secures the highest mechanical properties after completion of the heat-treatment process, but it also increases a tendency to the formation of cracks, produces high internal stresses and renders distortion more likely in the forgings than if the water had been hot. On the other hand, the use of boiling water will result in the attainment of lower mechanical properties, but there is then much less risk of crack formation and distortion, whilst the internal stresses may virtually disappear.³⁴

Clearly, a compromise is necessary and for this reason, it is customary to use warm (say, 40° C.), or hot (say, 70° C.) water for quenching, so as to achieve the desired level of properties (depending upon the alloy and purpose) and to minimize the risks of cracking and distortion by reducing the internal stresses. The quenching stresses locked up in a forging can be very high,^{10, 34} and whilst they are less troublesome in small forgings, it is generally accepted that when large forgings are to be extensively machined, the best practice is to heat-treat them in the roughly machined condition and employ warm water for quenching.

A further result that can be achieved by this procedure is to assist in reducing mass-effect. A good deal can be effected to ensure the highest possible strength in large forgings by completing the heavier machining before heat-treatment. The quenching stresses are not likely to be unduly disturbed by the subsequent light finishing machining, which helps to maintain the desired form of these components—a most important matter in modern construction.

Great accuracy in the control of temperatures is vital with most of these alloys, if they are not to be subjected to the danger of overheating during solution-treatment, which is conducted at temperatures just below the melting point of the eutectics of some of the constituents. There is, however, one alloy where some latitude is permitted, similar to

that allowed for the heat-treatment of steel.¹⁶ This is the alloy to specification D.T.D. 683 (see Table I, No. 11) which is the most recent to be developed and made generally available.

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472 *Hot Forging and Hot Stamping of Aluminium*

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THE HOT WORKING OF MAGNESIUM AND ITS ALLOYS.*

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SYNOPSIS.

Current practice in the rolling, extrusion, and forging of magnesium-base alloys in the U.K. is described, and special mention is made of the metallurgical factors which have led to the great advances in quality and economy of production which have taken place over about the last ten years. The importance of the direct-chill casting process is emphasized; stock so produced in the new zirconium-containing high-strength alloys can be hot worked over a wide temperature range, use of initial temperatures as high as 500°–520° C. permitting heavy reductions to be effected without failure. Short accounts are given of U.K. and U.S. development projects which have shown that modern magnesium-base alloys can be hot worked under drastic conditions similar to those which are applied to mild steel, and comments are made on some possible future lines of development. The compositions and properties of the principal alloys are given, and the effects of varying working conditions are indicated.

I.—INTRODUCTION.

DEVELOPMENT of magnesium-base alloys as engineering materials can be said to have started in 1909, when examples were exhibited under the name "Elektronmetall" at the International Aircraft Exhibition in Frankfurt by the former Chemische Fabrik Griesheim Elektron, one of the parent companies of the I.G. Farbenindustrie. Pioneering production and research were carried forward in Germany during the following years, greatly stimulated by the necessity to make fullest use of domestic resources in the 1914–18 war, and later by the growing demands of the aircraft industry for alloys with a specific gravity as low as 1.8. During this development period, the American Magnesium Corporation and the Dow Chemical Company started production in the U.S.A., and by 1936 an extraction plant was being operated in the U.K. by Magnesium Elektron, Ltd. Although magnesium alloys were manufactured in wrought form in the early years, serious progress has been made in establishing really economic hot-working conditions only

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during the last fifteen years, and the most productive period in this respect has been that since the early stages of the second World War.

In the present paper an attempt is made to review and discuss the metallurgical factors which have now emerged, and to show how magnesium alloys have progressed from a stage when they were regarded as somewhat freakish materials, which could be fabricated into wrought products only by careful "nursing", to one in which they are capable of withstanding drastic working conditions such as have been applied to mild steel for many years, and more recently to some aluminium-base alloys.

Magnesium and its alloys (with the exception of those having relatively large lithium contents¹) are capable of only limited cold deformation, and their fabrication into wrought products is therefore essentially a hot-working process. In part—for example, the cold rolling of thin sheet—the manufacturing technique here described does not strictly fall within the scope of this Symposium. Since, however, such techniques form such a minor part of the whole, brief mention of them will in fact be made for the sake of completeness.

At the same time, it must be emphasized that, with only a few exceptions, wrought magnesium-base alloys derive much of their strength from "cold" work in the strict metallurgical sense. That is, although deformation is effected at elevated temperatures, the material is nevertheless work-hardened. Sometimes a precipitation heat-treatment may be used to improve the properties, but this is not normal.

II.—CRYSTALLOGRAPHIC CONSIDERATIONS.

The close-packed hexagonal lattice structure of magnesium and its alloys is usually regarded as the most important single factor in determining both their working behaviour and the directionality of mechanical properties of the wrought products, and considerable research has been devoted to this subject.²⁻¹⁸ Among the metals in common engineering use, only zinc has a hexagonal structure, but here the practical implications differ, since zinc-base alloys are not used in wrought form in highly stressed applications. Thus, for zinc, crystallographic anisotropy is of little service importance, although it has an effect where bending and deep-drawing characteristics are concerned.

1. *Plastic Deformation.*

It may be useful here to recapitulate established theory on the deformation mechanisms of magnesium, which are generally accepted to apply also to its common alloys (the high-lithium alloys are excluded from this, however, as their structures are body-centred cubic).

At temperatures up to about 225°C ., plastic deformation of a single magnesium crystal takes place by slip on the planes of closest atomic packing—the basal planes (0001)—and in the most closely packed direction of the basal hexagon—the digonal axis I $[11\bar{2}0]$ (see Fig. 1, Plate LXVII).¹⁷ Above 225°C ., however, plasticity increases very markedly, since additional slip planes come into operation, namely the pyramidal planes I, type 1, $\{10\bar{1}1\}$, the direction of gliding again being the basal edge of the hexagon $[11\bar{2}0]$. Figs. 2 and 3 (Plate LXVII) ¹⁷ illustrate respectively this sudden increase in plasticity in a single crystal of magnesium under tension and in the forging of a polycrystalline alloy (in which, however, other modes of deformation may also operate).

Whilst basal and pyramidal slip are primary mechanisms of hot plastic deformation of magnesium and its alloys, mechanical twinning also plays an important part, and this takes place about pyramidal planes I, type 2, $\{10\bar{1}2\}$. It is believed that, in addition to the inherent effect of the twinning itself, deformation is further facilitated by generation of new basal slip planes (0001) in the process.

In the polycrystalline aggregate, all the deformation mechanisms just described may operate concurrently, since the mode applying in any one grain will be determined by its orientation. It is also probable that there are other modes, so far unknown, which come into operation in unfavourably oriented grains, resulting from complex systems of micro-stresses induced by interactions between the crystals of the aggregate.

It turns out in practice that magnesium and its alloys possess hot-working capabilities approximating to those of the face-centred cubic metals. As will be seen later, provided that working temperatures are sufficiently high, the amounts of deformation which can be effected after one heating operation are very large, and it is only under cold-working conditions that magnesium is at a disadvantage when compared with other metals.

2. Preferred Orientation and Directionality of Mechanical Properties.

It would be inappropriate in this paper to make a close examination of deformation textures, but it is perhaps useful to consider the broad outline of the subject.

Since basal slip is the principal mode of deformation, it is a general rule in all magnesium hot-working processes that the basal planes of the hexagons tend to become oriented in a direction substantially parallel to the flow of the metal. This is illustrated diagrammatically in Figs. 16 and 17.¹⁷

Twinning is produced by tensile stresses in the direction of the

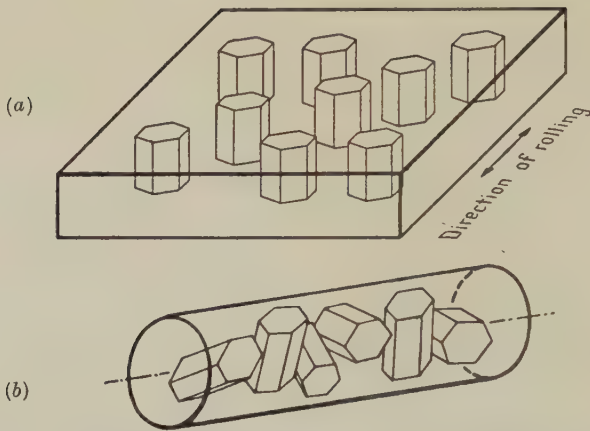
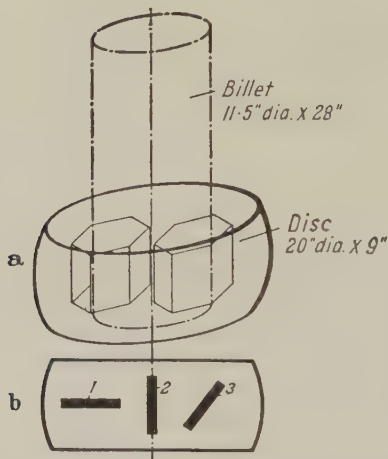


FIG. 16.—Diagrammatic Representation of Crystal Orientation (a) in Sheet, (b) in Extruded Bar.



Direction :	Elastic limit 0.02%, tons/in. ²			Proof stress 0.2%, tons/in. ²			Ultimate tensile stress, tons/in. ²		
	1	2	3	1	2	3	1	2	3
Tension	5.9	5.4	3.4	11.4	8.9	7.4	14.6	10.2	11.7
Compression	4.4	6.5	4.0	7.5	12.9	6.8	26.3	25.1	21.8
Compression/Tension	0.75	1.25	1.2	0.65	1.45	0.9	1.8	2.5	1.9

FIG. 17.—Relationship Between Tensile and Compressive Values as a Function of Crystal Orientation, exemplified on a disc of AZ855 forged in one direction only. (a) Diagram showing crystal orientation. (b) Section through the disc showing position of the test-bars.

hexagonal main axis and by compressive stresses at right angles to this axis; hence preferred orientation always results in maximum tensile proof (and ultimate) stress values being obtained in the direction of flow owing to resistance to deformation by twinning, whilst the compressive proof stress is at its highest at right angles to this direction. Properties illustrating this for a forged disc are shown in Fig. 17. In extrusions (Fig. 16 (b)) transverse tensile proof stresses are also low, since basal slip is aided in the transverse direction by the random orientation of the hexagonal main axes. In sheet low tensile properties would be found were it possible to measure them through the thickness, whilst the compressive proof stress would be considerably higher than in the plane of the sheet. There is, additionally, a difference between the tensile properties in the direction of rolling and at right angles to this direction in the horizontal plane (called longitudinal and transverse, respectively). In the usual case the weaker direction is longitudinal, tensile proof stresses sometimes being as much as 2 or 3 tons/in.² lower than they are transversely, whilst greater differences are shown in ductility. This type of directionality is occasioned by differences in angular scatter of the hexagonal bases in the two directions. More complex orientations are frequent, including double orientations and orientation changes from the centre to the surfaces of the sheet.

III.—ALLOY COMPOSITION.

Before reviewing the desirable characteristics of cast stock and considering the various working processes in detail, it will be useful to list and comment upon the principal alloys which have been, or are being, produced in the wrought state, and also to discuss the effects of impurities on working behaviour.

1. *Commercial Alloys.*

Pure magnesium is worked only rarely, and then only for certain special (mainly chemical) applications: to improve its engineering properties, it is always alloyed. As will be seen in Table I, the most important commercial alloys are based upon four main systems: magnesium-manganese, magnesium-aluminium-zinc, magnesium-manganese-rare earth metals, and magnesium-zinc-zirconium. A little manganese is always added to the second of these systems to improve corrosion-resistance. There is also an American impact-forging alloy containing tin and aluminium, also with a little manganese.

An important distinction between the magnesium-aluminium-zinc alloys and the others lies in the tendency of the former to hot shortness, increasing with aluminium and (especially) zinc contents. The reasons

TABLE I.—*Designations and Compositions of the Principal Magnesium-Base Wrought Alloys.*

D.T.D. and British Standard Nos. are quoted in Table IV (p. 488).

Alloy Designation	Alloying Additions						Usual Wrought Form
	Al, %	Zn, %	Mn, %	Ce, % †	Zr, %	Sn, %	
Elektron AM503 A.S.T.M. M1-Dow and AMC	1.5	} Sheet and extrusions.
	1.5	
Elektron AZ31 . . . A.S.T.M. AZ31X-Dow A.S.T.M. AZ31X-AMC	3.0 3.0 3.0	1.0 1.0 1.0	0.3 0.3 0.2	} Sheet and extrusions.
				
Elektron AZM . . . A.S.T.M. AZ61X*-Dow and AMC	6.0 6.5	1.0 1.0	0.3 0.2	} Extrusions and forgings.
				
Elektron AZ855 . . . A.S.T.M. AZ80X-Dow and AMC	8.0 8.5	0.4 0.5	0.3 0.2	} Press forgings and extrusions.
				
Elektron AM537 † . . Elektron AM6	2.0 2.0	0.5 6.0	Sheet and extrusions. Forgings for elevated-temperature service.
Elektron ZW2	2.0	0.7	...	Extruded tube (weldable by the Argonarc process). Sheet, extrusions, and press and impact forgings. Extrusions.
Elektron ZW3	3.0	0.7	...	
Dow ZK60	5.7	0.6	...	
A.S.T.M. TA54-AMC .	3.5	...	0.5	5.0	Impact forgings.

N.B.—In this paper the alloys are generally referred to by their "Elektron" designations, but for brevity the prefix "Elektron" is omitted.

* AZ61X, on account of its severe tendency to stress-corrosion, has been supplanted by AZ31X as the standard high-strength sheet alloy in the U.S.A. Elektron AZM has never been produced as sheet in the U.K. in more than very small quantities.

† Elektron AM537 was developed by the I.G. Farbenindustrie as a stress-corrosion-resistant alloy to replace AZM. Only small quantities have been produced in the U.K.

‡ Mischmetall.

for this are concerned with the low solidus temperature and intergranular weakness induced by the presence of eutectic in amounts which naturally vary with the alloying percentages. Thus, unless they have been given a really complete homogenization heat-treatment, the more highly alloyed materials have to be worked at relatively low temperatures (thereby restricting reductions which can be imposed in rolling and forging) if failure of the hot-short type is to be avoided ; in extrusion, speeds must be held down.

As will be seen later, magnesium-zinc-zirconium alloys excel the others in hot workability. This is mainly consequent upon the high solidus, permitting the use of working temperatures of around 500° C., and the very fine grain-size of the cast stock.

Interesting work is known to be proceeding on the magnesium-

lithium alloys¹; however, since the principal interest lies in their enhanced capacity for cold working (at room temperature), only this mention of them is made in the present paper.

2. *Effects of Impurities.*

In hot-working behaviour, magnesium is very insensitive to impurities within the limits normally occurring in the commercial range of alloys, namely up to about iron 0.03, copper 0.005, nickel 0.0015, tin 0.005, lead 0.005, sodium 0.025, calcium 0.01, and silicon 0.01%. Indeed, in the authors' experience, only calcium of those mentioned has been known to cause trouble, and then only in experiments in which alloying percentages were deliberately introduced. This element produces slight increases in strength properties of magnesium-zinc-zirconium alloys in the wrought condition, even with additions of less than 0.05%, but above this figure hot-working behaviour is impaired. In the U.S.A., calcium is added to the magnesium-manganese alloy to refine the grain of cast rolling slabs and to improve ductility. If, however, the amount is not carefully confined to 0.1–0.2%, there is risk of hot shortness.

IV.—STOCK FOR HOT WORKING.

Of the main hot-working processes applied to magnesium alloys, sheet rolling and impact forging make the greatest demands upon quality and structure of the stock, whilst these factors are of less importance in extrusion and hydraulic press die-forging in which deformation can be slower and maximum lateral support is given to the stock in the early stages of working. Bar and section rolling and preforming operations in hydraulic press forging can be said to occupy intermediate positions in this range. In addition to working speed and lateral support, temperature is also significant, particularly from the point of view of deterioration in preheating.

1. *Sheet Rolling Slabs.*

Up to 1939 it was almost universal practice to produce rolling slabs from iron-chill-cast cylindrical billets by extrusion; the slab itself was not cast. The reasons for this lay in the relatively poor casting characteristics and coarse columnar cast grain-size of AM503, and the presence of a hot-short intergranular phase in the aluminium- and zinc-containing alloys, such as AZM and AZ31. In that year, however, an iron book-mould was developed, giving AM503 slabs as large as $24 \times 24 \times 3$ in., which, after a reasonable amount of surface machining, were sufficiently sound and isotropic to roll satisfactorily. Such cast slabs were not entirely free from defects, and bridging cavities (Fig. 11, Plate LXIX)

were sometimes present, but usually these welded-up in the rolling operation. These slabs were used for nearly the whole of the U.K. sheet production in AM503 throughout the recent war, and are still in use. During the same period, satisfactory slab moulds were also developed in the U.S.A., but it was only when direct-chill processes had been successfully evolved that cast, rather than pre-extruded, slabs came into anything approaching general application in that country. At that time also it became usual in the U.S.A. to add 0.1–0.2% calcium to AM503 (and other) type alloys, one of the main functions of this being to produce a relatively fine equi-axed grain structure in the interests of rollability. However, much trouble was experienced in the U.K. on imported U.S. sheet through the effect of calcium causing cracking of oxy-acetylene welds.

Coming now to present-day practice in this country, all the zirconium-containing alloy slabs are produced by semi-continuous direct-chill casting. They are free from macro-cavities and contain only very small amounts of distributed microporosity, and thus give none of the troubles arising from such defects as were experienced with similar material cast in the ordinary book-moulds. Internal oxide and nitride formation in preheating due to “outcropping” porosity had been particularly troublesome. The direct-chill-cast slabs are effectively free from oxide inclusions, and a particular advantage lies in the avoidance of segregations of intermetallic compounds or impurities. In the crude form, the slabs show a small amount of “bleeding” of inverse segregate and some edge folding, but these defects are readily removed by machining all surfaces. Afterwards, the slab is pickled and finally inspected, particular watch being kept for casting cracks which, however, occur only rarely under normal conditions. The standard slab has dimensions of $42 \times 14\frac{1}{2} \times 4\frac{5}{8}$ in. after machining, and weighs roughly 180 lb. : in the future, however, it is planned to increase this weight very substantially, casting up to a thickness of 8 in. A photomicrograph illustrating the typical structure of direct-chill-cast ZW3 alloy is given in Fig. 4 (Plate LXVIII). As will be seen later, these slabs can be broken-down to 0.2 in. blanks after a single heating to 500° C. without any edge or surface cracking.

The amount of β phase in ZW3 alloy is very small, and the influence of direct-chill casting on its distribution is therefore of minor importance. In aluminium- or aluminium- and zinc-containing alloys, however, this factor becomes significant, especially from the point of view of homogenization time. The advantage in this respect presented by the newer casting method can be seen from Figs. 6 and 7 (Plate LXVIII), in which the structures of book-mould and direct-chill-cast AZM alloy cylindrical

billets of similar diameter have been etched to outline the phase. In the development of the rolling of a magnesium-5% aluminium alloy some years ago, fine and uniform dispersion of the grain-boundary phase proved of great value, and direct-chill-cast slabs of good rollability were produced.

2. Stock for Cogging and Bar and Section Rolling.

A description of a development project involving cogging and bar and section rolling of magnesium alloys is given later. Such processes are not yet applied commercially, but if they were, the initial "ingot" would be direct-chill cast.

3. Extrusion Billets.

Extrusion billets are made in diameters ranging from 2 $\frac{7}{8}$ to 12 in., and the usual cast length is 30-36 in.; they are fully machined before extrusion. The zirconium-containing alloys are all direct-chill cast.

Mention should be made of the old I.G. Farbenindustrie "water-sink" casting process, wherein billets were poured in thin-walled moulds; these, after a period under a hood furnace for the settling of impurities, were slowly lowered into water to effect the chill. This process was used extensively for billets required for extrusion into forging stock, and gave a sound product. It was, however, dangerous, and stripping was difficult.

4. Forging Stock.

Most forging stock in AZ855 and AZM alloys is made by pre-extrusion, thus obtaining a broken-down structure better suited for forging operations. Even then, however, these alloys leave much to be desired in forgeability under the hydraulic press; under the hammer or mechanical press, AZ855 is unworkable, whilst AZM can be processed only very cautiously. The reason for this lies in the intergranular weakness resulting from the relatively high aluminium and zinc contents. It is interesting to note that experience has shown that such hot shortness is not eliminated by a complete solution heat-treatment as evidenced under the microscope, and real improvement is not achieved without extremely lengthy (and uneconomic) homogenization periods in which diffusion of the aluminium and zinc throughout the α phase can take place.

With the zirconium-containing alloys, it has been possible to turn over completely from pre-extrusion to the use of direct-chill-cast forging stock which can be effectively processed under either the press or the hammer. A similar forging performance (although in some respects still inferior to that of the zirconium-containing alloys) is given by

AM503 and (A.S.T.M.) TA54 alloys, but forgings in these alloys do not give the highest strength properties. Experience in certain types of ZW3 alloy impact forging has shown that the use of cast rather than extruded material presents advantages associated with the randomly oriented grain structure, as compared with the marked anisotropy of extruded bar.

V.—SHEET ROLLING.

Of the main working processes used for magnesium alloys, sheet rolling involves the largest number of separate operations and makes the greatest demands upon process control. Two of the most important factors calling for careful attention are concerned with preheating conditions and the necessity of maintaining the right temperature in the sheet if the maximum reduction is to be accomplished in any one rolling stage. Additionally, the use of hot rolling down to quite thin gauges makes it necessary to be especially meticulous in control of roll "pick-up" and in the removal of any foreign matter adhering to the sheet.

Ansel and Betterton¹⁹ have given an excellent review of American rolling practice, and in this section of the present paper it will be necessary only to devote detailed attention to the two alloys which have been, or are being, manufactured in sheet form in quantity in this country, namely, the binary magnesium-manganese alloy AM503 (corresponding to the American M1) and the zirconium- and zinc-containing alloy ZW3 (see Table I).

It must be emphasized that with all except the really "difficult" rolling alloys (e.g. AZM), the rolling schedule is principally governed by the plant available. It has been found that the best way to roll magnesium alloys, both from the point of view of economy and results, is to use the highest practicable rolling temperature and to "hit them hard". The attainment of the first of these requirements depends largely upon the type of reheating furnace available and its position with respect to the mill, and the second is naturally a function of the power and robustness of the rolls. The details given in this paper for AM503 and ZW3 alloys represent those which are typical when using the best type of plant so far available in the U.K. for magnesium on a production scale. Given even more suitable plant, shortening and other improvements of the rolling schedule would undoubtedly be possible. A fairly detailed description is given, since this is a matter on which there has been little publication.

1. *Preheating the Slabs.*

Both AM503 and ZW3 alloy cast slabs are preheated to a temperature of 490°–510° C., which, with existing furnaces, represents the best com-

promise between two opposing considerations : namely, the desirability of using the highest possible temperature to achieve maximum reduction, and the avoidance of excessive oxidation.

Preheating furnaces are usually of the electric, forced-circulation, semi-continuous conveyor type, the slabs being loaded in at one end and withdrawn from the other after the preheating period, passing through on a slowly moving conveyor. Apart from obvious safety measures to prevent even local overheating of the stock, or contamination with foreign matter which will promote oxidation or other harmful reaction (contact with aluminium is especially undesirable), the use of the shortest possible soaking time consistent with temperature uniformity is the most important factor. This involves adoption of furnace zone temperatures (especially at the loading end) considerably higher than 500° C., and makes it more necessary to guard against local overheating; but it pays ample dividends in restricting general superficial oxidation. Special furnace atmospheres such as SO₂ are not used, mainly because of their unpleasantness. Where necessary, however, a protective coating can be applied to the slabs before loading into the furnace.

The tendency to oxidation, or the local fusion of low-melting-point constituents, naturally varies from alloy to alloy. In this respect AM503 is particularly good and the high aluminium-containing alloys are especially difficult. Even if the latter are given an apparently thorough solution-treatment before preheating, there is always risk of fusion and burning of small residual pockets of low-melting phases. Like AM503, ZW3 alloy is entirely safe from this latter point of view, but its relatively high zinc content leads to an increased tendency to general surface oxidation.

2. Breaking-Down.

Typical breaking-down schedules for AM503 and ZW3 alloys are detailed in Table II. It will be seen that the slab is rolled down to 0.2 in. blank (or thicker, according to the gauge of the final sheet) in about 10 passes; the finishing temperature is usually of the order of 300° C., but this depends upon the type of mill and rolling speed used (usually pass-back or reversing two-high mills, with speeds of 200–250 ft./min.). Actually, the finishing temperature—provided it is not so low as to lead to cracking—is normally of little consequence; if, however, finished plate is being manufactured in a single breaking-down operation it has to be controlled in the interests of mechanical properties.

In the first few passes, the slab is rolled across its width until this has been increased to the desired width of the final sheet plus appropriate

TABLE II.—*Typical Breaking-Down Rolling Schedules for AM503 and ZW3 Alloys.*

Slab Size	Screw-down Settings, in.		Nominal Reduction per Pass, %	
	AM503	ZW3	AM503	ZW3
AM503 : 24 × 16 × 2 $\frac{7}{8}$ in.	2.60	3.50	9.6	24.4
	2.10	2.65	19.2	24.3
	1.70	2.10	19.0	20.8
ZW3 : 42 × 14 $\frac{1}{2}$ × 4 $\frac{5}{8}$ in.	1.30	1.55	23.5	26.2
	0.90	1.20	30.8	22.6
	0.60	0.75	33.3	37.5
	0.40	0.47	33.3	37.4
	0.30	0.30	25.0	36.2
	0.25	0.21	16.7	30.0
	0.22	0.15	12.0	28.6

The slabs are broken-down to the width of the final sheets plus allowances of 1 $\frac{1}{4}$ in. per side for AM503 and $\frac{3}{4}$ in. per side for ZW3.

edge allowances. It is then turned and all subsequent rolling is in the new direction. The passes are usually determined on the basis of maximum pinch consistent with safe power loading, but towards the end of the breaking-down flatness of the blank is the primary consideration.

It has been found best to use flood lubrication of hot 2% soluble oil; this helps to control roll "pick-up" and to maintain steady roll-temperature conditions.

Mainly in consequence of the coarse columnar grain-size, AM503 slabs can give trouble in breaking-down, partly through poor surface condition, but more particularly by severe edge cracking. ZW3 alloy normally shows no sign of either surface or edge cracking. It is standard procedure with this alloy to roll to a width very little more than the width of the finished sheet, since no intermediate side shearing is necessary before the final cutting to width.

As shown in Fig. 5 (Plate LXVIII), the cast structure of the ZW3 slab is converted to a fully wrought condition in the breaking-down and, provided that the finishing temperature is correct, high mechanical properties can be achieved in the blank.

3. Sheet Rolling.

The blank, which may be up to 30 ft. in length, is sheared into pieces of a size governed by the dimensions of the finished sheet, and for the zirconium-containing alloy the only metal scrapped at this stage is that at the extreme ends, leading to recoveries of 90–95%. AM503 has

to be side sheared to remove edge cracking. Depending upon the adequacy of control of "pick-up" by lubrication and roll wipers, the blanks may or may not be brushed and/or pickled before reheating for further rolling.

The furnaces in current use for reheating generally have shelves holding perhaps up to 20 blanks stacked horizontally, there being individual doors for each shelf or sets of shelves. Such a type gives relatively slow heating, and there is considerable scope for improvement here. Quite apart from the question of production rate, quick heating

TABLE III.—*Typical Rolling Schedules for AM503 and ZW3 Alloy Sheet.*

Alloy	Finished Gauge, S.W.G.	Rolling Stage	Initial Temp., ° C.	Initial Thickness, in.	Final Thickness, in.	Reduction, %	Number of Passes
AM503	10	First hot rolling	450	0.250	0.142	43.2	2
		Final cold rolling	...	0.142	0.128	10	6
	14	First hot rolling	450	0.220	0.150	31.8	1
		Second hot rolling	385	0.150	0.089	40.6	2
		Final cold rolling	...	0.089	0.080	10	5
	18	First hot rolling	450	0.220	0.105	52.4	3
		Second hot rolling	385	0.105	0.054	48.5	5
		Final cold rolling	...	0.054	0.048	11	6
	ZW3	Final hot rolling	480	0.250	0.128	48.8	3
		First hot rolling	480	0.250	0.125	50.0	3
			480	0.125	0.080	36.0	3
		First hot rolling	480	0.200	0.085	57.5	4
			450	0.085	0.058	31.8	4
			430	0.058	0.048	17.3	4

is desirable to restrict oxidation and prevent excessive grain growth, which, unless the percentage reduction in subsequent sheet rolling is high, will result in sub-standard mechanical properties in the finished material. In this connection it may be mentioned that a continuous-type flash-annealing furnace has been successfully used, but the ultimate ideal would probably be a furnace holding the blanks (or intermediate sheets) in loose vertical racks, with really effective forced circulation, the atmosphere being raised to temperature in a separate heating chamber.

In hot sheet rolling, the main essential is to achieve the highest possible reduction in thickness per reheat, and this is best effected by using the highest practicable starting temperature with only a few, but really heavy, passes. As will be seen from Table III for example,

0.25-in. ZW3 blank is reheated to 480° C. and rolled down to sheet of 10 S.W.G. (0.128 in.) in three or four passes. Flood lubrication with 2% soluble oil is again used to control "pick-up".

This hot rolling is repeated according to the desired finished gauge, but as the sheet becomes thinner, both the reheating and the rolling problems become greater. It is true, of course, that the thinner the sheet, the quicker will it come up to temperature, but also the quicker can it oxidize or overheat. As far as the rolling is concerned, the thinner the sheet becomes, the more quickly does it lose its heat, so limiting reduction. (It must be remembered that the heat capacity of magnesium alloys is low.) As can be seen in Table III, it is usual to reduce reheating temperatures progressively as the sheet comes down in gauge, and also to omit the use of rolling lubricant at a certain thickness. The passes must be so adjusted as to give an intermediate rolled sheet which is sufficiently flat to permit easy charging into the furnace for the next reheat. Finishing temperature in such operations is 300°–200° C. according to gauge, and the limiting factor here relates to the avoidance of cold cracking which, if it is allowed to occur, is of the 45° shear type. Pack rolling of two sheets has been applied successfully, but is somewhat troublesome in regard to sticking and surface finish.

The attainment of high strength properties in the final sheet depends upon the degree of cold work which has been made to occur in the hot rolling. The higher the temperature, the heavier is the reduction per pass necessary to produce this cold work, and the conditions already mentioned for 10 S.W.G. sheet are satisfactory in this respect. As the gauge becomes thinner and the rolling temperatures are necessarily lower, the minimum reduction for achievement of desired properties naturally falls. Thus for 20 S.W.G. sheet, for which the final rolling is carried out over the temperature range 300°–60° C., a minimum reduction of about 12% is satisfactory: this is to be compared with a minimum of about 40% for 10 S.W.G. material.

The foregoing remarks on finish-rolling apply to current practice for ZW3 alloy. AM503 alloy is usually finished by a 7–10% cold rolling, following an intermediate anneal, but the hot- or warm-finishing technique may also be applied to this alloy.

It must be admitted that a really economic finishing process for sheets thinner than 18 S.W.G. has not yet been evolved. In principle hot rolling is the most desirable, since it allows maximum reduction with achievement of good mechanical properties. Unfortunately, short of the provision of really specialized plant, this presents practical difficulties, not only from the point of view of heat retention, but also as regards maintenance of a uniform roll camber—a factor of great im-

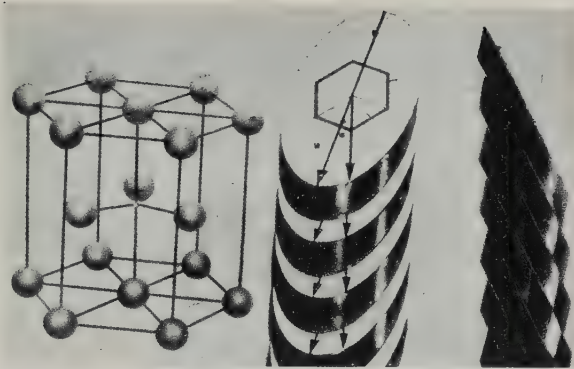


FIG. 1.—Atomic and Slip Model of a Magnesium Crystal.

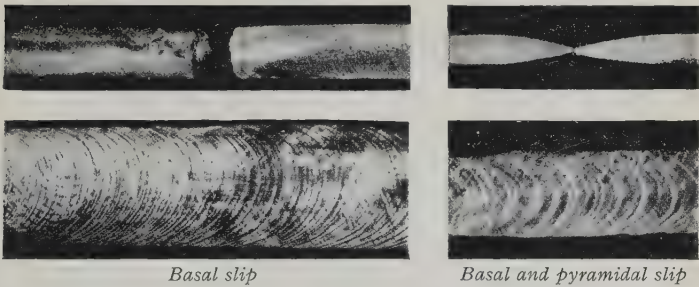


FIG. 2.—Slip Bands of Cold- and Hot-Elongated Magnesium Crystals.



FIG. 3.—Sudden Change in the Plastic Properties of Magnesium Alloy AZM.

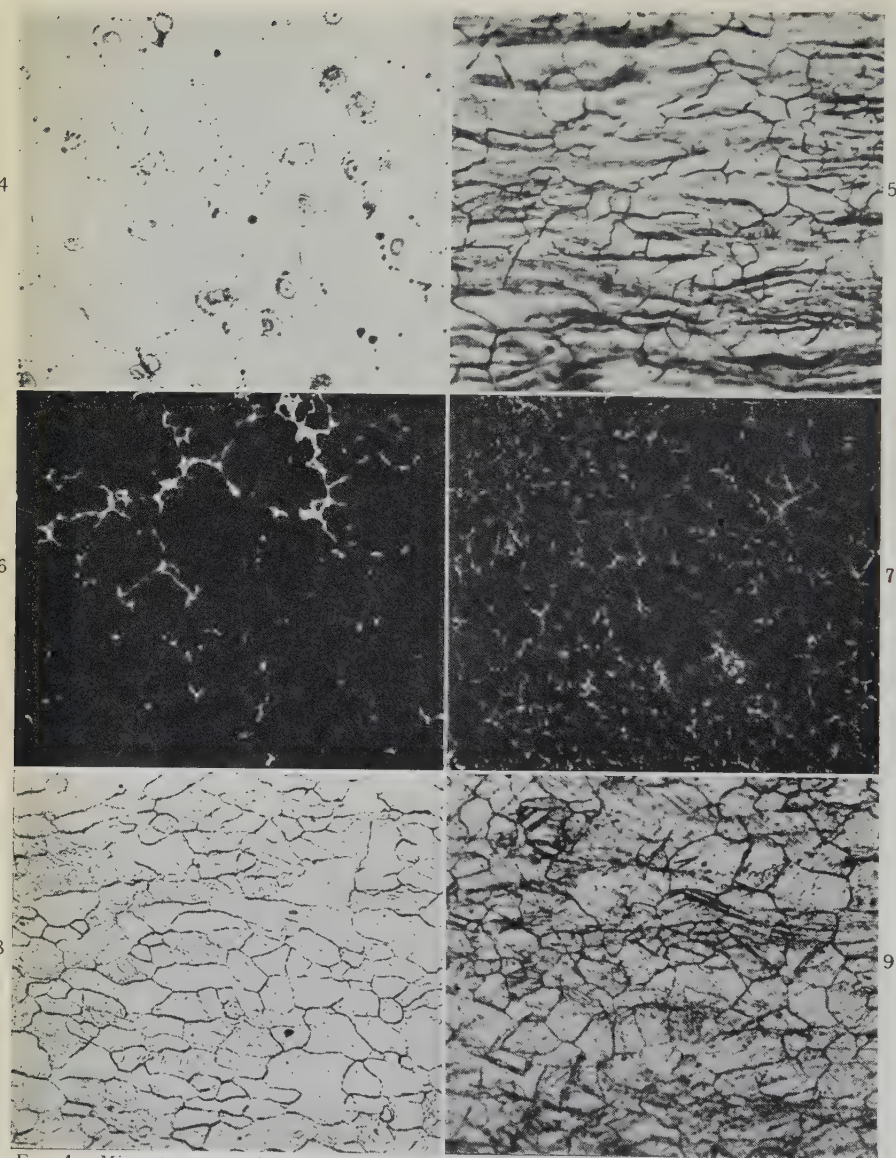


FIG. 4.—Microstructure of ZW3 Alloy Rolling Slab Cast by the Semi-Continuous Direct-Chill Process. $\times 250$.

FIG. 5.—Typical Longitudinal Microstructure of ZW3 Alloy 0.25-in. Blank from the Breaking-Down Operation. $\times 650$.

FIGS. 6 and 7.—Comparison of β Phase Dispersion in AZM Alloy 12-in. Billets Cast (Fig. 6) in a Book Mould, and (Fig. 7) by the Semi-Continuous Direct-Chill Process. $\times 30$.

FIGS. 8 and 9.—Typical Longitudinal Microstructures of AM503 (Fig. 8, $\times 250$) and ZW3 (Fig. 9, $\times 300$).



FIG. 10.—Rolling of a Zirconium-Containing Magnesium Alloy Ingot in the Cogging Mill at Middlesbrough.

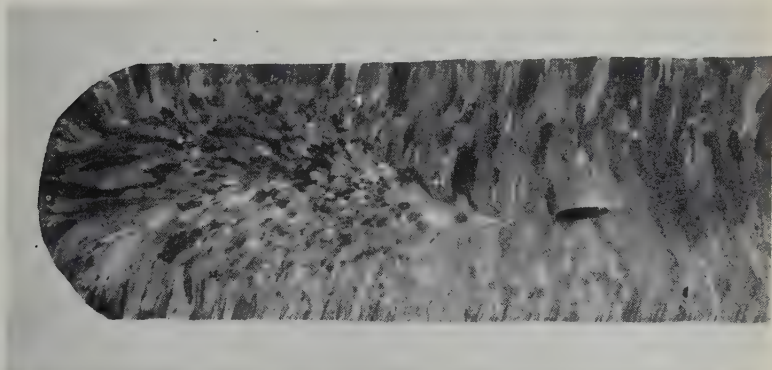


FIG. 11.—Part of a Macro-Etched Transverse Section of an AM503 Alloy Rolling Slab Cast in a Book Mould. Approx. $\frac{1}{2}$ size.

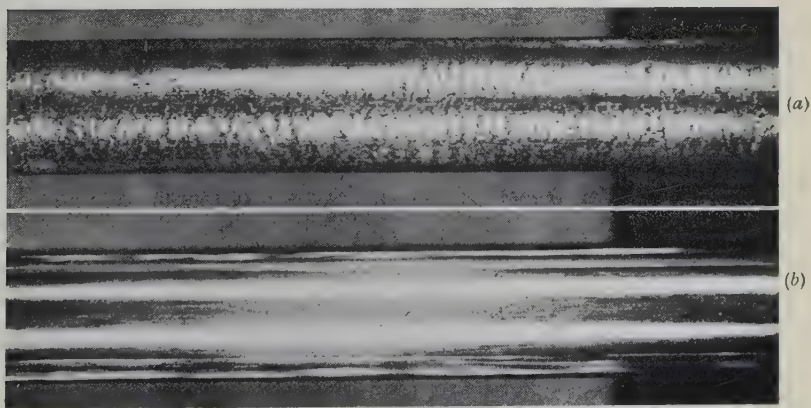


FIG. 12.—AM503 Alloy Bar Extruded at 8 ft./min. (a) and 60 ft./min. (b), Showing the Resultant Difference in Surface Condition. Approx. full size.

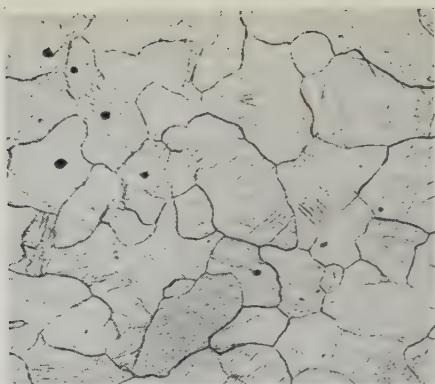


FIG. 13.—Typical Transverse Microstructure of AM503 Alloy Extrusion. $\times 150$.

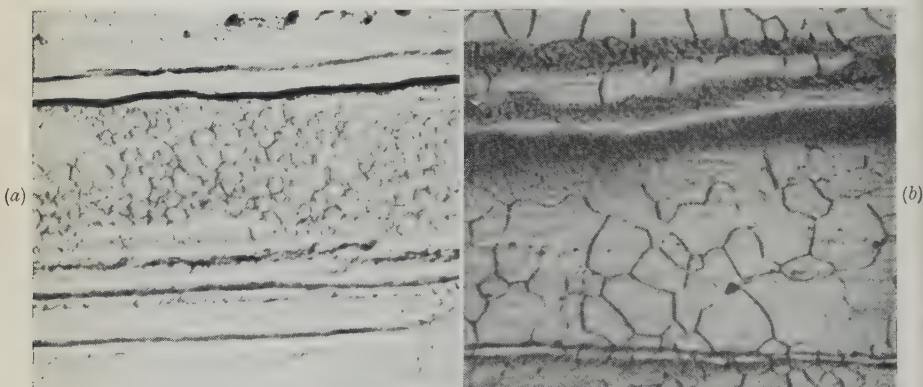


FIG. 14.—Typical Longitudinal Microstructures of Extruded ZW3 Alloy: (a) Very fine grain-size (approx. 0.003 mm.) and little zirconium precipitation, giving high properties; (b) relatively coarse grain-size (approx. 0.008 mm.) and much zirconium precipitation, giving medium properties. $\times 1200$.

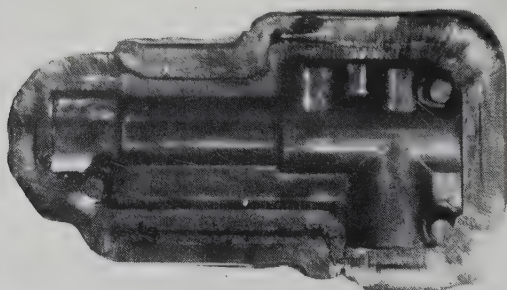


FIG. 15.—Valve-Body Forging, still carrying the die flash.

portance in the rolling of thin sheet if a satisfactory shape is to be achieved. However, it has proved possible to go some way in the application of hot rolling right down to 20 S.W.G., and there is no doubt that the difficulties will eventually be overcome completely.

Since magnesium alloys have a low heat capacity on account of their low specific gravity, and since heat retention is of such great importance for the achievement of heavy reductions, it is naturally very desirable to operate with rolls at the highest possible temperature in all rolling stages. However, with existing plant, experience has shown that provision of special roll heaters involves practical difficulties (particularly concerning roll-camber control), which become the greater as the sheet becomes thinner, and, on balance, such provision is best omitted. Indeed, with thin sheets, rolls may even have to be cooled, in the interests of good shape.

Sheets from the last rolling stage, although bowed, have a good shape and are free from buckles. They are sheared to finished dimensions and then finally flattened. Up to comparatively recently, roller levelling was almost universal, but is now becoming superseded by new methods which are under development and which do not result in the drastic reductions in longitudinal proof stress which are induced (through twinning under compression) by roller levelling. Typical microstructures of AM503 and ZW3 sheet are shown in Figs. 8 and 9 (Plate LXVIII).

Finally, the sheets are cleaned by pickling, with or without a brushing operation, and given a protective treatment in one of the two alternative chromating baths.

Percentage recoveries from machined slab to finished sheet vary from about 40 to 80%, according to gauge and alloy. The higher figures are obtained on the thicker material; and, for a given gauge, ZW3 is substantially better than AM503 in this respect.

Typical tensile properties of sheets in the two alloys are given in Table IV.

4. Future Developments.

In the preceding Sections, an account has been given of current rolling practice in this country utilizing existing plant of the older type. Given an adequate consumer demand, however, there is no doubt that magnesium alloys could be produced by continuous rolling methods, and this has been proved successfully in a development project carried out in the U.S.A.¹⁸ AZ31 alloy slabs, $108 \times 17 \times 7$ in., weighing 825 lb., were broken-down on a two-high 27×48 in. reversing steel mill with edging rolls, and further rolled to 0.075 or 0.050 in. *without* reheating on a four-stand tandem train of four-high finishing mills ($16\frac{1}{2}$ and

TABLE IV.—*Typical Tensile Properties of the Wrought Magnesium Alloys.*

Except where otherwise indicated, the lower figures in the ranges are the D.T.D. Specification minima.

Alloy and Form	D.T.D. Specn. No.	B.S. Specn. No.	Tensile Properties		
			0.1% Proof Stress, tons/in. ²	U.T.S., tons/in. ²	Elongation, % on 2 in.
AM503					
Sheet	118A	1353	6-10	13-18	5-14†
Extrusions	142A	1355	8-13	15-20	4-10
Extruded tubes	737	1357	8-10*	15-17	4-6
AZM					
Extrusions (>3 in.)	259A	1354	11-14	17-22	10-18
Extrusions (>3 in.)	749	1354	9-12	14-19	8-16
Extruded tubes	348A	1356	9-11*	17-20	8-12
Forgings	88C	1351	10-13	18-20	8-14
AZ855					
Press forgings	88C	1351	10-14	18-22	8-14
ZW2					
Extruded tubes (Argonarc weldable)	Pending	...	11-15*	17-22	3-8
ZW3					
Sheet (18 S.W.G. and thicker)	626 ‡	...	11-14	17-20	8-18†
Sheet (19 and 20 S.W.G.)	626 ‡	...	10-13	16-19	...
Sheet (thinner than 20 S.W.G.)	626 ‡	...	9-12	15-17	...
Extrusions (medium strength):	622 ‡	...			
(Rounds, squares, hexagons, and simple sections)	622 ‡	...	14-17	20-23	10-25
(Difficult sections)	622 ‡	...	12-15	17-21	10-15
Extrusions (high strength, >3 in.)	733 §	...	17-21	23-26	8-14
Press forgings	619	...	13-15	19-22	8-14
Impact forgings	729	...	11-14	17-20	8-12

* D.T.D. Specifications 737 and 348A do not specify figures for proof stresses; however, minimum values for 0.2% proof stress of 9 and 10 tons/in.², respectively, are given for information only. A 0.2% proof stress mandatory minimum of 12 tons/in.² is proposed in the draft D.T.D. Specification for ZW2 tube.

† For AM503 sheet 12-15 S.W.G. and 16 S.W.G. and thinner, the ductility requirements are cold-bending radii of 8T and 6T, respectively. For ZW3 sheet 16 S.W.G. and thinner, the ductility requirement is a cold-bending radius of 6T.

‡ As amended 7 July 1949.

§ These highest-strength extrusions are not available for all sections.

38 × 48 in.) with an up-coiler. The slabs were taken down to $\frac{3}{8}$ in. on the reversing mill in 17 passes in times as short as 2 min. (with speeds up to 600 ft./min.), and the sheet came out of the four-stand tandem as fast as 1245 ft./min. The secret of success here lay in the heat generation involved in rolling at such high speeds. In the U.K., on sheet-rolling tests have yet been carried out upon such an ambitious scale, but it can be recorded that rolling slabs have been successfully broken-down upon a two-high reversing mill with edging rolls at speeds as high as 400 ft./min.

In Germany during the recent war development along somewhat different lines was envisaged.¹⁹ It was planned to lay down four-high rolling mills with large-diameter and comparatively slowly driven rolls capable of withstanding extremely heavy pressures. Such a scheme may have had potential advantages, but in the authors' opinion the ultimate ideal is more likely to lie in the use of high-speed rolling in which the generated heat is probably utilized more efficiently.

VI.—COGGING AND BAR AND SECTION ROLLING.

A development carried through successfully some years ago in collaboration with Messrs. Dorman Long and Co., Ltd., and Darlington and Simpson Rolling Mills, Ltd., demonstrated the operation of principles similar to those shown more recently in U.S. work on continuous sheet rolling. After preliminary experiments on the section rolling of both normally cast and direct-chill-cast stock at speeds as high as 500–600 ft./min., an ordinary steel ingot mould was borrowed, and ingots in the zirconium- and zinc-containing alloy ZW3 (and others) were successfully cast, weighing 945 lb. after machining. These were preheated to 480°–500° C. in a coke-oven-gas furnace and, immediately after a shift on mild steel, they were clogged-down with only the *single heating* to both 2 × 2 in. billet and 12 × $\frac{3}{4}$ in. sheet bar (approximate lengths 300 and 135 ft., respectively) by the same operatives, and under similar conditions, as for the steel. Apart from the inevitable inclusions of mill scale and other foreign matter, these products were of good quality. After shearing into suitable lengths, the billet was rolled into light angle and glazing sections at the high speeds used for steel. Heat generation in such severe working had been strikingly demonstrated in the early experiments by the fact that in one example material was put into the finishing rolls at a temperature as low as 175° C. and, without reheating, was taken down to a light window-frame section, emerging at about 300° C. Naturally, the tolerances on the finished sections were not up to aircraft materials standards, but they were adequate for

ordinary structural purposes, as also were the mechanical properties, although strength figures were somewhat lower than for extrusions. In this latter connection, it is worth mentioning that a motor-vehicle wheel-rim section which was produced (in this case directly from cast stock) showed an advantage over extrusions in that there was little or no longitudinal-transverse directionality of properties. Photographs illustrating this work and typical mechanical properties of the sections rolled directly from cast stock are given in Figs. 10 (a) and (b) (Plate LXIX) and Table V, respectively.

TABLE V.—*Tensile Properties of Light Sections Rolled from Cast Stock.*

Alloy	0.1% Proof Stress, tons/in. ²	U.T.S., tons/in. ²	Elongation, % on 2 in.
ZW3	10-15	16-19	12-18
AM503	7-9	14-16	5-12

These experiments were of interest in pointing the way to the possibility of the cheap production by rolling of sections in magnesium alloys. As an extension of this idea, one could imagine a cogging mill operating on large direct-chill-cast billets to produce rolling slab, extrusion billet, and forging bar. Such a process, if it could be realized, would be expected to lead to considerable production economies, particularly by eliminating machining costs which are of increasing significance as the size of the product decreases.

VII.—EXTRUSION.

In the U.K., extruded bars, sections, and tube are made from billets of 2½–12 in. dia. on presses varying in power over the range 600–3500 tons; normal maximum pressures on the billet are 30–50 tons/in.² Extrusion technique is generally similar to that for aluminium-base alloys, but, amongst special considerations, die design is one of the most important. While opinion on this subject is by no means unanimous, it is the authors' general experience that with most alloys the best results are obtained by using a short bearing length and a sharp die entry, the only lead-in radius being that produced by wear. Billet temperatures in the range 250°–450° C. are used, depending on the alloy and type of extrusion, and preheating is mainly carried out in electric through-type furnaces. Container temperatures should be identical with, or only slightly higher than, billet temperatures. Whilst no important innovations have been applied to the production of bar and section, two important advances have been made in respect of tube extrusion:

namely, the successful use of "port-hole" dies for AM503, ZW3, and ZW2 (imperfect welding is experienced with AZM and other aluminium-containing alloys), and the application of piercing in the extrusion of large-diameter tubes in ZW3 alloy. All magnesium alloy tube manufacture was previously from bored billets.

In briefly describing extrusion conditions, it will be well to consider each alloy separately, since the factors vary widely with composition.

1. *AM503 Alloy.*

This binary magnesium-manganese alloy is very soft at extrusion temperature and only relatively low pressures are required. The most important single consideration in its extrusion is that of using high speeds in the interests of good surface condition. As shown in Fig. 12 (Plate LXIX), low speeds of the order of 10 ft./min. lead to a very poor surface, whilst high speeds, say 50–100 ft./min., overcome this difficulty. Extrusion temperatures usually vary from 250° to 350° C., according to the reduction and billet length. A photomicrograph showing the typical structure of extruded AM503 alloy is shown in Fig. 13 (Plate LXX), and tensile properties (which are relatively insensitive to extrusion conditions) are given in Table IV.

2. *AZM and AZ855 Alloys.*

For these aluminium- and zinc-containing alloys, the main consideration is the avoidance of the speed cracking that results from hot shortness, which is particularly marked in unhomogenized billets. Extrusion temperatures mainly vary from 250° to 400° C., but permissible speeds only rarely exceed about 12 ft./min. It is perhaps worth mentioning here that during the war the I.G. Farbenindustrie developed two methods of increasing the permissible extrusion speeds;^{20, 21} these were the use of water-cooled dies to hinder temperature rise of the worked material, and of differential preheating along the length of the billet. For the latter, a special furnace was designed to give a considerably higher temperature at the front of the billet than at the back; this permitted easy starting of the extrusion and also progressively higher speeds towards the end.

Like AM503, AZM and AZ855 alloys are relatively insensitive to variation of extrusion conditions as affecting mechanical properties (Table IV).

Extrusions in these alloys may contain relatively large quantities of β phase and Al_4Mn particles, and there is some evidence that such heterogeneity may lead to weakness in fatigue. For high-duty applica-

tions, it is therefore desirable to solution-treat the billets and to control the manganese content to the minimum consistent with good corrosion-resistance.

3. ZW2 and ZW3 Alloys.

The zirconium- and zinc-containing alloys ZW2 and ZW3 are identical in extrusion characteristics, although the lower zinc content of the former (necessitated by weldability considerations) leads to

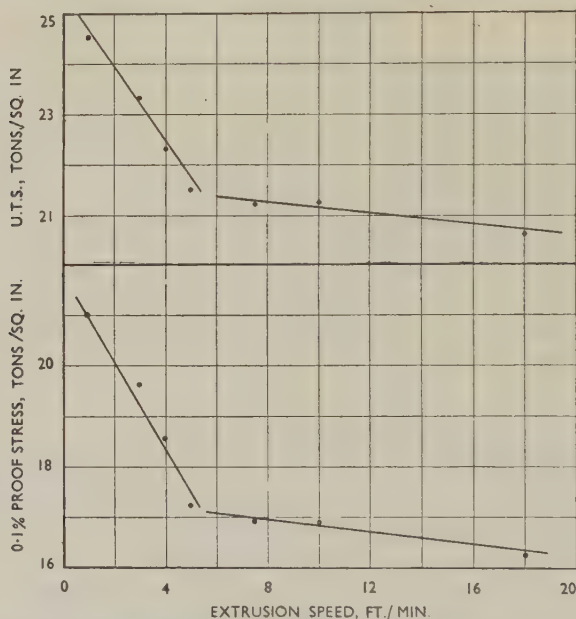


FIG. 18.—Effect of Extrusion Speed on the Tensile Properties of ZW3 $\frac{3}{4}$ -in.-dia. Bar. Extruded at 320° C.

slightly lower mechanical properties. These are high-strength alloys, but, unlike AZM and AZ855, the unhomogenized cast billet contains only very small quantities of the second phase, and, with a solidus temperature of about 590° C., it is therefore possible to extrude them at high speeds without any risk of cracking. The second important difference is the fact that in regard to mechanical properties (Fig. 18 and Table IV) the zirconium alloys are sensitive to billet preheating time, temperature, and extrusion speed. Broadly, if the time is long and the temperature and speed high, tensile properties comparable with those of the older alloys are obtained, and the grain-size is fairly large. If the time is short and the temperature and speed low, the high

properties associated with an extremely fine grain-size are achievable. Thus the alloys can be used for extrusion in two ways: advantage can be taken of high speed to cheapen production whilst obtaining mechanical properties of a medium level; or low speeds and close control of the preheating conditions can be applied, leading to the attainment of properties higher than have been available before. The harmful effect of long billet preheating time is due to precipitation of zirconium from solid solution; this results apparently in a reduced work-hardening response for given conditions of extrusion, and therefore in lower properties.

Strength sensitivity to temperature and speed (the latter is itself essentially a temperature effect) is in fact to be explained almost wholly on cold-working and grain-size considerations. Photomicrographs of high- and medium-strength extrusions are shown in Fig. 14 (Plate LXX); and in Fig. 18 typical curves are given to illustrate the relation between speed and tensile properties for $\frac{3}{4}$ -in.-dia. round bar.

The zirconium-containing alloys are comparatively new, and much further development work remains to be carried out, particularly from the point of view of establishing variation of properties with section type and dimensions.

An important advantage possessed by ZW2 and ZW3 extrusions lies in their high compressive proof stresses which result from inhibition of twinning when the grain-size is very fine.

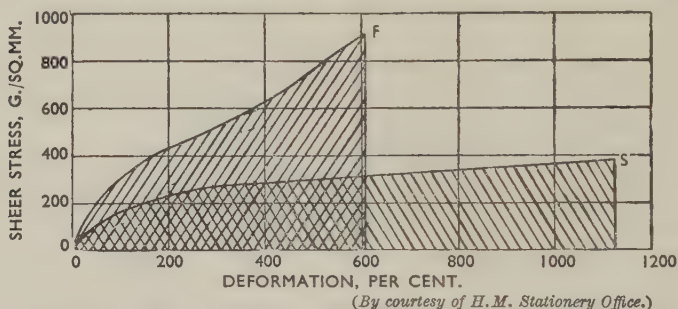
Mention should be made here of the American finding²² that increased zinc contents of the order of 5–6% (e.g. in Dow ZK60) give a somewhat reduced sensitivity to extrusion speed in respect of mechanical properties.

VIII.—FORGING.

For many years, magnesium alloy forgings have been manufactured under hydraulic presses, mechanical presses, and hammers, but it is only comparatively recently that it has been possible to make high-strength components under the severe deformation conditions applying in the latter two processes. The comparatively soft materials, AM503 and TA54 (the American tin- and aluminium-containing alloy), have always been forgeable under the hammer, but until the zirconium-containing alloy ZW3 became available, the highest-strength material was that containing 8% aluminium (AZ855), and this has to be forged under the hydraulic press. Even then, unless the stock is really sound and homogeneous, it may give cracking trouble through hot shortness.

It has been argued that magnesium alloys are best forged under a slow-acting press on the assumption that the total energy of deformation

which can be applied without rupture is constant at any given temperature, and (see Fig. 19²³) that it is possible to achieve greater percentage deformation in any one forging stage at lower rather than higher speeds. It was also said that under slow working conditions recovery and recrystallization have a better chance of keeping pace with deformation. (It may well be that this latter point accounts to a great extent for the increased deformation at low speed shown in Fig. 19.)²⁴ However, it is now clear that an overall economic advantage can result from forging under the hammer, using the highest possible reduction per stage. The hydraulic press does, however, score from the point of view of structural homogeneity and of mechanical properties of the



(By courtesy of H.M. Stationery Office.)

FIG. 19.—Stress-Strain Diagram for Magnesium Crystals Deformed at 250° C. For the curve marked *F* the speed of deformation was 100 times that for the curve marked *S*, but the area enclosed by the two curves (a measure of the work done on the material) is the same.

finished forging. During slow deformation, recrystallization seems to be more complete, and there is a greater possibility of temperature control—usually a progressive reduction—to help in putting the right amount of cold work into the material to achieve maximum strength figures.

It will be remembered that the preferred orientation of the hexagonal lattice which develops in plastic deformation results in substantial directionality of properties. Generally, the tensile properties are highest in the direction of metal flow, whilst the compressive figures are higher at right angles to this direction. It has been suggested¹⁷ that such directionality is least when the forging temperature is lowest, but, in the authors' experience, the only practical step of any real value which can be taken is to introduce as much variation as possible into the direction of forging in various stages, as illustrated in Fig. 20.¹⁷ It is, however, sometimes possible to exploit the occurrence of directionality of properties, particularly where it can be arranged that the maximum figures are obtained in the direction which is also that of principal stress in service.

Whether the forging stock is cast or extruded, preheating or reheating temperatures vary from about 500° to 300° C., and the furnaces should preferably be of the electric forced-circulation type permitting rapid heating to high temperature without oxidation. In this country, hydraulic presses varying in capacity from about 250 to 12,000 tons have been used, whilst in America there is an 18,000-ton press in operation; during the war, the Germans were actually in process of installing a 30,000-ton machine.²⁰

Impact forging is carried out using the same mechanical presses and hammers as for aluminium-base alloys. The general features of die design applicable to aluminium-base alloys are also applicable to magnesium alloys, and lubricants used—often graphite in tallow—are similar.

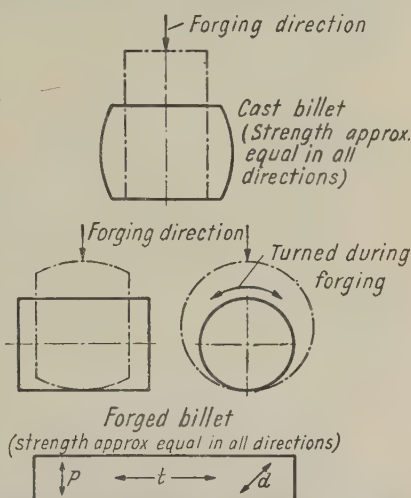


FIG. 20.—Diagram Illustrating the Process of Forging in Alternating Directions.

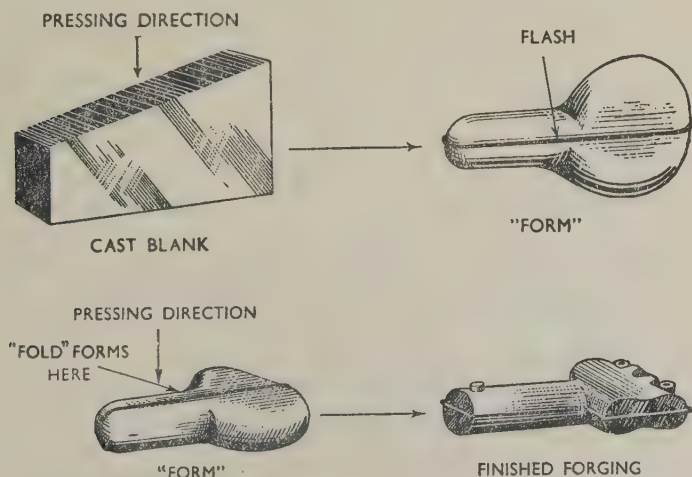


FIG. 21.—Sequence of Pressing Operations in the Production of a Press-Forged Valve Body.

1. Hydraulic-Press Forging.

As an illustration of press forging, the production and properties of a valve body will be briefly described. This component was made in

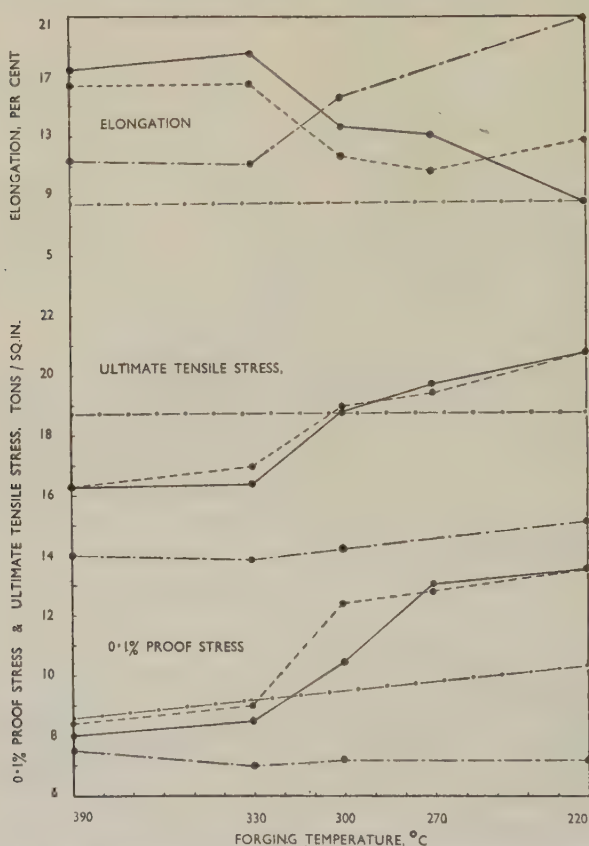


FIG. 22.—Effect of Forging Temperature on the Longitudinal Tensile Properties of Magnesium Alloy Valve-Body Forgings.

KEY.

- — — — ● Magnesium-3% zinc-2% cadmium alloy.
- - - - - ● Magnesium-3% zinc-2% cadmium-0.7% zirconium alloy.
- — — — ● Magnesium-3% zinc-0.7% zirconium alloy (ZW3).
- ● Magnesium-8% aluminium-0.4% zinc alloy (AZ855).

large quantities during the war in an aluminium- and zinc-containing AZ855 type of alloy, and the die was adopted for extensive experimental work on zirconium-containing alloys. Fig. 21 shows the

sequence of pressing operations, and Fig. 15 (Plate LXX) is a photograph of the final forging still carrying the die flash. In standard production of the aluminium-containing alloy, the die-cast blank was preheated to 385° C. and pressed in a pair of forming dies on a 250-ton machine, the dies being kept at about 300°–320° C. by means of gas-ring heaters. After sawing off the flash and grinding smooth, the form was reheated to 385° C. and placed in the lower half of the finishing die on a 1000-ton press (working speed 24 in./min.), the upper half die then being “bedded-on”. During this operation, a small fold developed in a position shown in Fig. 21, and this was removed by chipping and grinding before reheating again to 385° C. and giving the final squeeze in the same dies.

The curves shown in Fig. 22 relate longitudinal tensile properties with forging temperature for AZ855, ZW3, a magnesium–zinc–cadmium–zirconium alloy and the same alloy without zirconium, and, amongst other things, they illustrate the effects of this alloying element. Curves of similar form were obtained for transverse tensile properties.

2. Impact Forging.

Extensive work on the impact forging of the zinc- and zirconium-containing alloy ZW3, starting from both cast and extruded stock, has been done in the last few years, and both simple and complex components have been successfully made in the same dies as those used in the production of aluminium-base alloys.

One of the simplest forgings²¹ is shown in Fig. 23. This was made from a cast blank, $9\frac{1}{2} \times 4\frac{1}{2} \times 2$ in., which was preheated to 450° C. and forged under the open hammer to 3 in. dia. The “use”, $4\frac{1}{4}$ in. in length, was reheated to 430° C., “dummied” and given two blows in the dies. After reheating to 430° C., the “use” was given two further blows. Finally, the piece was reheated to a temperature varying from 325° to 460° C. and finished in three blows. Table VI gives the tensile properties obtained after forging at the various temperatures. These figures show some increase in strength with decreasing forging temperature, but the differences are not so great as they would be in hydraulic-press forging. This indication of reduced temperature-sensitivity may be partly connected with less perfect distribution of work through the piece when impact forged than when press forged. The

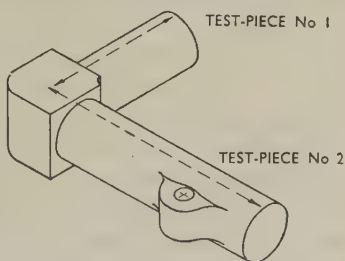


FIG. 23.—A Typical Impact Forging of Simple Type Made in ZW3 Alloy.

TABLE VI.—*Tensile Properties of a Typical Impact Forging in ZW3 Alloy Made at Different Temperatures.*

Forging Temp., ° C.	Test-Piece No. (see Fig. 23).	0·1% Proof Stress, tons/in. ²	U.T.S., tons/in. ²	Elongation, % on $4\sqrt{A}$
325	1	13·5	18·3	17
	2	11·6	17·9	11·5
440	1	11·3	17·2	9
	2	11·2	15·8	...*
460	1	7·8	17·8	17
	2	11·1	17·2	...*

* Fractured in grips.

Note.—Test-piece No. 1 was a tensometer specimen.

parts from which the test-bars were taken might not have experienced the full effects of the deformation in the impact-forged piece, whereas a similar press-forged piece might well have been more affected.

IX.—GENERAL.

An attempt has been made in this paper to show the progress in the hot working of magnesium alloys, the period concerned being roughly that since 1939. The picture here presented differs greatly from the orthodox pre-war view of the subject, in which magnesium alloys were thought of as being hot-workable only by very special, slow, and expensive methods.

It is interesting to remark that in essence the reasons underlying this change are very simple; they are these: (a) the provision of better cast stock, (b) the availability of more suitable plant, and (c) the provision of alloys of finer grain-size and more useful metallurgical characteristics.

Considering these a little more closely, (a) comprises not only the solution of the problem of direct-chill casting magnesium alloys, but also the understanding, which was lacking earlier, of the important part played in hot working by prior homogenization of the aluminium-containing alloys. The structural uniformity of direct-chill-cast material is so well known an advantage for any working operation that it requires no further comment here.

The high speeds and reductions which are now seen to be possible derive partly also from (b), since, for example, working at high temperatures (not far from incipient fusion ranges) is possible only with well-instrumented electric furnaces of the right type, and heavy rolling reductions cannot be attempted if powerful mills with suitable handling equipment are not freely available. Considering

therefore the present-day performance of the alloys which were produced before the war, one can see that the pre-war inhibitions were mainly due to inadequate technological development at that time, and perhaps also to an excessive preoccupation with hypothetical difficulties thought to derive from the simple fact that the metal is hexagonal in structure.

Of the three factors given above, however, the last is probably the most important, and the potentialities of the magnesium alloys containing zirconium have led to the most technically useful developments in the working field. Not only are the grain-size and recrystallization characteristics important influences, but it is fortunate that the alloys developed have high solidus temperatures, permitting heavy deformations to be imposed in temperature ranges up to about 520° C. These alloys not only hot work well, but they have improved mechanical properties, and this has provided a stimulus to the investigation of some of the matters considered here.

It is, however, unfortunately true that full advantage cannot yet be taken of all the lessons which have been learned from some of the newer developments, since consumption does not yet justify, for example, continuous strip rolling. Particularly in the U.K., the potentialities of wrought magnesium alloys are governed by general economic, rather than by technical, considerations.

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THE HOT WORKING OF COPPER AND 1229 COPPER ALLOYS.*

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SYNOPSIS.

After a brief consideration of the nature of hot working and some observations on its application in the processing of copper and copper alloys, the more important of the metallurgical and operational factors associated with it are discussed. Various tests for assessing hot-working properties and their applicability are described. The hot workability of various types and qualities of copper and of copper alloys such as the brasses, aluminium bronzes, nickel silvers, cupro-nickels, and silicon bronzes are discussed with particular reference to composition as related to constitution, and to the effect of additional alloying elements and impurities. Finally, brief reference is made to some of the more important features, chiefly metallurgical, of the most widely used industrial hot-working processes, such as rolling, extrusion, piercing, and forging, as applied to materials of the kind described.

I.—INTRODUCTION.

ALTHOUGH the term hot working is quite commonly used to indicate the processing or manipulation of metals and alloys at temperatures above normal, its more precise and correct meaning is working at temperatures appreciably above the recrystallization temperature. When material is hot worked in this defined sense, therefore, it shows no work-hardening effects on cooling down to normal temperature. If the material is constitutionally complex or undergoes thermal transformations of any kind, its hardness after hot working may be sensibly affected by cooling conditions, but any further hardening which may accrue in this way, subsequent to hot working, is quite unrelated to work-hardening. In short, true hot working differs from cold working in that material so processed is substantially free from the strain-hardening effects which characterize the latter, and, moreover, the mechanism of deformation is different.

In general, when a metal is stressed it usually deforms elastically at first, and if the application of stress is continued, it deforms plastically. At room temperature plastic deformation of copper, for example, is

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associated with work-hardening and distortion of the crystal structure, and with increasing deformation a stage is ultimately reached when no further hardening or lattice distortion occurs. As the temperature of working is raised, the degree of work-hardening for a given amount of deformation decreases and the stress required to effect a defined amount of deformation decreases with increase of temperature.

Single crystals of copper and its solid-solution alloys and also crystals of all the face-centred cubic metals, deform at room temperature by slip on planes of densest atomic packing in the directions of closest packing. Since there are four families of such planes, and three possible slip directions in each plane, there are twelve possible slip systems, and that which operates under any given conditions is the one most favourably disposed with respect to the applied load. In polycrystalline material, however, there is interaction between neighbouring grains at grain boundaries, and slip deformation is more complex. A theoretical analysis by Taylor¹ has indicated that the stress required to deform a polycrystalline mass is about five times that required to deform a single crystal to the same extent.

When slip takes place on any one plane, lattice distortion and work-hardening occur in the neighbourhood of that plane, so that further slip is possible only on parallel planes separated by intervals greater than a certain limiting amount. It has been shown² that the magnitude of the limiting slip-plane interval increases with temperature and, moreover, there is evidence which indicates that at elevated temperatures slip can take place on many other planes. In addition to slip deformation, a certain amount of deformation can occur by viscous flow, or relative displacement of grains at grain boundaries. The relative amounts of deformation taking place by these two mechanisms varies with temperature. At normal temperatures slip mechanism is dominant, but with increasing temperature there is a progressively increasing proportion of viscous flow, so that at the so-called "equi-cohesive temperature" deformation can occur equally by slip or viscous flow, and at still higher temperatures the latter predominates.

The decrease in work-hardening and in deforming stress with increase in working temperature can be explained on the basis of these three observations, that is, an increase in slip-plane interval, the change in character of the slip mechanism, and the occurrence of appreciable viscous flow at grain boundaries. Little information, however, is available concerning the changes which take place in metals and alloys when they are worked at relatively high temperatures, and it is, therefore, not yet possible to generalize about the exact nature of the mechanisms of the changes in crystal structure involved in the deformation

under these conditions, which, provided the temperature is high enough, can be carried out extensively without any appreciable work-hardening.

II.—GENERAL OBSERVATIONS.

In the manufacture of semi-fabricated forms of copper and copper alloys, such as plate, sheet, strip, tube, rod, sections, and wire, and in the subsequent production therefrom of finished articles, both hot- and cold-working operations are employed. Leaving out of account purely local or domestic considerations such as the availability of plant, which are not basic or fundamental issues, the factors determining the choice between hot and cold working are essentially those of economics, which involve size of output, and applicability or suitability. Since it is possible in the hot state to deform more rapidly and with less power than it is in the cold state, the former, on the grounds of economics, would on a first or primary consideration commend itself. But there are, of course, other considerations, such as the relative suitability of a given material for manipulation by hot or cold processes as determined by its composition and constitution, the form in which the metal or product is finally required, and the finish and properties needed. For these and other reasons it is not possible to generalize on the relative merits of hot and cold working either from the viewpoint of economics or technicalities, but a broad indication of the position as it affects copper and copper alloys can be given.

It is, and has been for long past, an almost universal practice to hot work copper, in all its various grades, such as tough-pitch, deoxidized, oxygen-free, arsenical, &c., in the form of plates, sheet, strip, and rod, for this metal, in the absence of any abnormal or unusual features, can be very easily and readily rolled, forged, and otherwise hot worked over a wide range of temperatures and presents no serious technical problems. Whether or not the hot rolling is continued throughout, except possibly for additional light operations such as flattening or straightening, or is stopped short as a preliminary process to subsequent finishing by cold rolling, in the case of sheet or strip, or cold drawing, in the case of rod, depends on what is required of the finished product in respect of gauge tolerance, surface finish and appearance, and physical and mechanical properties.

It has also long been the common practice to fabricate hot, either in the early stages of processing, or to final forms, those alloys of copper such as the brasses, and various types of bronzes, which, by virtue of their content of zinc or other alloying elements, are beyond the limit of the α range, for not only are they, in fact, much more readily hot-

workable than the corresponding α alloys, but most of them cannot easily be cold worked to any great extent.

Over the last two decades the tendency has been to adopt hot working to an increasing extent for the early processing stages, where the size of output justifies the outlay on plant, and, in particular, hot rolling of relatively large ingots of alloys of the α type in preference to the former practice of commencing with much smaller ingots and cold rolling throughout. This, indeed, is one of the most apparent changes in recent years in the technology of wrought copper alloy production.

III.—FACTORS ASSOCIATED WITH HOT WORKING.

The two items covered by the term hot workability, as usually understood, are (i) the temperature range over which a metal or alloy is ductile, malleable, and workable, and (ii) its resistance to deformation at temperatures within that range, and both are measurable under defined conditions. Although any metal or alloy can be conceived as having an intrinsic hot-working value, so far as its composition is concerned, the measurement or assessment of this value is complicated by such factors as crystal structure, soundness, segregation, and others, whether in a sample being subjected to one or another form of hot-workability test or in a full-size ingot or billet being processed. Moreover, different tests do not necessarily provide results of the same order, and it does not follow that a material which hot works well in one operation will do so equally well in another of a different type. While it is, therefore, scarcely possible to give a quantitative expression which would have any value or usefulness in relation to the term hot workability, nevertheless as a result of experiment and experience a good deal of information has been accumulated about the hot working of industrial alloys and of the effect of many of the factors associated with it.

• The subject of composition itself is a large one and is dealt with separately, if only briefly and in the broadest outline, in Section V, but a few observations of a general kind are relevant in considering those factors associated with hot workability and hot working, of which composition is one of the most important. It is convenient to consider composition under three divisions: (i) the primary or basic composition of the alloy, that is, 70 : 30 brass, 90 : 10 aluminium bronze, 80 : 20 cupro-nickel, &c.; (ii) the addition, if any, of smaller amounts of other alloying elements such as, for example, lead in a 60 : 40 brass, or deoxidizers, such as phosphorus, in copper; and (iii) fortuitously occurring elements in the form of impurities.

In any particular system, if more than one phase occurs, the hot

workability of copper-rich alloys is characteristically associated with their structural constitution. The hot workability, as measured by either the ductile temperature range or the ease of working within that range, of those alloys which consist entirely of the α phase is, in general, not so good as that of pure copper. Alloys consisting of the $\alpha + \beta$ and β phases, however, can be easily hot worked over a wide range of temperatures, and in this connection it should be realized that alloys possessing an $\alpha + \beta$ structure at room temperature consist largely, or even entirely, of β at the temperature of hot working. The capacity of $\alpha + \beta$ and β alloys for cold work, however, is much less than that of the α alloys, and decreases as the proportion of β , with its body-centred cubic lattice, increases.

To such alloys as the brasses, aluminium bronzes, cupro-nickels, and silicon bronzes, additions of other metallic elements, up to about 1 or 2%, are sometimes made, to obtain particular or special properties. Most of these additions are metallic elements, and, with the common exception of lead, are, in the amounts usually added, wholly soluble in the solid state, and generally they have little significant effect on hot workability.

Low-melting-point impurities of limited solid solubility, such as lead and bismuth, for example, and elements forming low-melting-point compounds, when present in the α alloys in quite small proportions, generally have a pronounced adverse effect on hot workability, although larger amounts may be present in β alloys with much less effect. Smith³ has suggested that whether or not hot shortness occurs in a metal or alloy containing a small quantity of liquid phase depends upon surface-energy relationships which may be expressed in terms of the interfacial tensions between liquid and the solid grains. The interfacial tensions may be compared by the measurement of dihedral angles of the liquid inclusions. For lead in α brass the dihedral angle is small and increases slightly with zinc content, with an abrupt increase when the β phase first appears. Where the wetting angle is zero, the liquid metal will rapidly penetrate grain boundaries and cause the alloy to be brittle, although it is considered that under tensional forces, liquid penetration leading to rupture along grain boundaries may occur with small positive wetting angles, though not where the wetting angle is large, as, for example, in β brasses at the normal temperature of hot working. Voce and Hallows,⁴ in the course of observations on the embrittlement of copper by bismuth, calculated that the minimum bismuth content necessary to cause hot shortness was just sufficient to form a monatomic layer on the grain boundaries, which would seem to indicate a wetting angle of zero for this pair of metals in the hot-brittle range, although there are alternative explanations.⁵

Although the inherent hot workability of a material itself may be of a relatively high order, both the degree of deformation possible without cracking and the range of hot-working temperature can be affected to a marked degree by the quality and condition of the casting, in respect of crystal configuration and the distribution of gaseous or contractional unsoundness and segregation. In general, a casting of fine uniform grain made by the best casting practice is likely to be workable over a wider range of temperature than a casting of coarse, uneven grain-size, especially if the latter is accompanied by unsoundness and insoluble impurities. The configuration of the cast structure is also important in determining to what extent a small amount of an impurity is likely to cause hot shortness, and the considerable discrepancies between the various experimental results and industrial experience, such as, for example, the tolerance limit for lead in the α brasses, may well be associated with pronounced differences in the cast structures to which they relate.

In alloys in which, because of rapid cooling, the phase relationships differ appreciably from the equilibrium condition, the homogeneity, and hence the hot workability, may often be improved by a soaking or homogenizing treatment before working. Segregation in casting is not generally found in the copper alloys, other than the tin bronzes, with which this paper is not concerned, for freezing ranges in the α and β phase fields are short. In the copper-zinc alloys, the longest freezing range occurs at about 67% copper, and slight segregation in these alloys often leads to the presence of β in the casting. It has been suggested in an earlier paper⁶ that this segregation may contribute in some measure to the need for close control of casting conditions and grain-size to ensure the successful hot rolling of 67 : 33 brass. However, in alloys just within the $\alpha + \beta$ phase field the small proportion of β present under equilibrium conditions is generally found to be located at the grain boundaries, and there seems to be some evidence that this adversely affects hot rolling.⁷

Industrial hot-working operations vary in severity in respect of the conditions to which the material is subjected during deformation. The hot piercing of billets in the production of tube shells is one of the most severe, for it involves very complex stresses which are at one stage mainly tensional, and the product may be adversely affected by a partial breakdown of the structure even in alloys considered to be readily workable at the temperature of operation. In extrusion, on the other hand, where the metal is confined, the stresses are mainly compressional, and this process is one which allows the maximum latitude of conditions in the material being processed. Crystal size and formation is another relevant factor, but usually it is not nearly of so much consequence, so

far as hot working is concerned, in extrusion as it might be in an ingot for hot rolling. Again, the presence of impurities or constituents leading to some measure of hot shortness, as, for example, lead in an $\alpha + \beta$ brass, has a much more marked detrimental and limiting effect in hot rolling and stamping than in extrusion. In rolling with unsupported edges considerable tensile forces operate which may give rise to edge cracking in some materials under certain conditions, but the use of edging rolls may greatly reduce such cracking.

In most hot-working operations the initial temperature is the most significant, that is, the temperature at which deformation of the cast structure commences. If the details at this stage are correct, it is generally possible to continue hot working over a range of temperature

TABLE I.—*Hot-Rolling Temperatures for Copper and Copper Alloys.*

Material	Nominal Composition		Initial Hot-Rolling Temperature, °C.
	Copper, %	Other Elements, %	
H.C. Copper . .	99.9	0.03–0.05 oxygen	750–900
D.O. Copper . .	99.9	0.03–0.05 phosphorus	750–900
Arsenical Copper . .	99.0	0.05 oxygen, 0.4 arsenic	800–900
D.O. Arsenical Copper .	99.0	0.05 phosphorus, 0.4 arsenic	800–900
Gilding Metal . .	95.0	5.0 zinc	750–850
Cartridge Brass . .	70.0	30.0 zinc	720–830
Two-and-One Brass . .	67.0	33.0 zinc	780–820
65 : 35 Brass . .	65.0	35.0 zinc	720–830
Basis Brass . .	63.0	37.0 zinc	720–830
Nickel Silver . .	62.0	18.0 nickel, 20.0 zinc	880–920
Muntz Metal . .	60.0	40.0 zinc	680–800
Leaded Brass . .	62.0	36.75 zinc, 1.25 lead	750–830
Naval Brass . .	62.0	37.0 zinc, 1.0 tin	680–800
Aluminium Bronze . .	93.0	7.0 aluminium	800–900
Silicon Bronze . .	96.0	3.0 silicon, 1.0 manganese	750–850

and down to temperatures at which working could not have been started without damage.

The choice of initial working temperature and other conditions for fabricating an alloy on a manufacturing scale depends on both the metallurgical characteristics of the alloy, and the conditions most appropriate for the economic employment of the plant, and, if the material is to be used in the hot-worked condition, on the structure and properties desired in the product. To limit working pressures and power requirements to a minimum, temperatures in the upper part of the ductile range would naturally commend themselves, but these may be too high for the tools and other machine parts involved to withstand. A lower temperature, therefore, might be selected if the saving resulting from prolongation of die or roll life, for example, more than

counterbalances the cost of the extra power required. Possible surface damage caused by heavy oxide scales formed at high temperatures is another consideration which in some circumstances will affect the choice of initial hot-working temperature. With such materials as the $\alpha + \beta$ copper alloys, it is possible to take advantage of the ease with which many of them can be worked over a wide temperature range, and so select working temperatures yielding the structure and properties required in the product.

The foregoing brief analysis indicates some of the more important factors involved in determining hot-working conditions, concerning which it is clearly not possible to generalize. It will be appreciated, therefore, that the information given in Tables I and II concerning initial hot rolling and extrusion temperatures for some representative varieties of copper and some typical copper alloys, is illustrative rather than definitive, and although it will be applicable in many circumstances, others may involve departures from the temperatures given.

TABLE II.—*Extrusion Temperatures for Copper and Copper Alloys.*

Material	Nominal Composition.		Form	Initial Temperature Ranges for Extrusion, ° C.
	Copper, %	Other Elements, %		
H.C. Copper . . .	99.9+	0.03-0.05 Oxygen	Rod, section	850-900
D.O. Copper . . .	99.9+	0.03-0.05 P	Tube	850-900
D.O. Arsenical Copper . . .	99.5	0.03 P, 0.4 As	Tube	850-900
Gilding Metal . . .	85.0	15.0 Zn	Tube, rod	840-860
70 : 30 Brass . . .	70.0	30.0 Zn	Tube, rod	820-840
Admiralty Brass . . .	70.0	29.0 Zn, 1.0 Sn	Tube	800-820
Nickel Silver . . .	65.0	18.0 Zn, 17.0 Ni	Tube	850-900
Muntz Metal . . .	60.0	40.0 Zn	Rod, tube	680-720
Naval Brass . . .	62.0	37.0 Zn, 1.0 Sn	Rod, section	680-720
Hot-Stamping Brass . . .	57.0	41.5 Zn, 1.5 Pb	Rod, section	680-720
Free-Turning Brass . . .	57.0	40.0 Zn, 3.0 Pb	Rod, section	680-720
High-Tensile Brass . . .	57.0	37.0 Zn, 3.0 Al, 2.0 Mn, 1.0 Fe	Rod, section	760-780
High-Tensile Brass . . .	58.0	38.0 Zn, 0.5 Pb, 1.0 Fe, 1.25 Mn, 1.25 Sn	Rod, section	760-780
Nickel Brass . . .	44.0	44.0 Zn, 2.0 Pb, 10.0 Ni	Rod, section	760-780
Aluminium Bronze . . .	90.0	10.0 Al	Rod, section	820-840
Nickel-Aluminium Bronze . . .	91.0	7.0 Al, 2.0 Ni	Rod, tube	820-840
Silicon Bronze . . .	96.0	3.0 Si, 1.0 Mn	Rod, tube	840-860
Cupro-Nickel . . .	80.0	20.0 Ni	Tube	850-900
Cupro-Nickel . . .	68.0	30.0 Ni, 1.0 Fe, 1.0 Mn	Tube	850-900

IV.—HOT-WORKABILITY TESTS.

The most reliable way of ascertaining how easily or otherwise a metal or an alloy can be hot worked by any particular manufacturing procedure is, of course, to process it under actual plant conditions, since all the variables involved, such as composition, size, shape, and crystal structure of the ingot, as well as those relating to the operation itself,

such as speed of deformation, temperature, pressure, and so forth, are simultaneously covered. This course, however, is not feasible in investigational work in which large numbers of experimental materials may be under consideration, and to enable rapid, preliminary assessments to be made of hot-working behaviour, much more conveniently and inexpensively, if less completely, than would be possible on a full scale, various types of test have been devised. Most of these are capable of providing useful and helpful indications, especially when information is obtained from several and not just one of them. However, because such tests do not reproduce all the various conditions obtaining in industrial hot-working processes, nor other factors in the material itself arising from size and other considerations which might affect hot workability, both caution and experience are needed in interpreting results. In addition to specific tests calculated to provide information about hot workability by yielding measurements of some particular property or properties—however uncertain the connection between the two may be—certain operations such as hot rolling and extrusion, for example, when carried out on a small or laboratory scale, can give useful results, if, in their interpretation, full and careful consideration is given to those factors the significance of which may be influenced by the scale of operation.

Tensile-strength values and the measure of ductility as evidenced by elongation and reduction of area determined by short-time testing at elevated temperatures, afford, for the materials covered by this paper, some general indication of hot workability, in as much, for example, as low tensile and high ductility values over a range of temperature suggest ease of manipulation in respect of power requirements and absence of hot shortness. Conversely, high tensile strength and low ductility might be taken as indicating the need for high pressures or loads and the presence of hot shortness or a limited capacity for deformation without cracking or rupturing. Such test results, however, admit of only the broadest interpretation and have even less significance in regard to hot workability when they relate to alloys of different kinds. Much more information concerning hot workability can be obtained from tensile tests if they are sufficiently extensive to yield complete details of the stress-strain relationship at various temperatures and of the effect of varying rates of deformation, but such tests would be far too lengthy to be of use for a quick preliminary assessment of hot-working possibilities.

Notched-bar impact tests, which have been used for the detection of brittleness or hot-short ranges in non-ferrous alloys,^{4,8,9} appear to be very sensitive, especially when the hot shortness is associated with the

presence of a brittle or liquid phase at the grain boundaries. As the amount of energy absorbed depends also, for example, upon whether or not the test-piece is broken, low values are obtained with materials that are very soft and ductile as well as with those that are brittle, and, therefore, it is clear that results from tests of this kind call for extreme caution in their interpretation in indicating behaviour in hot-working operations.

Hot bend tests are used to some extent in evaluating hot workability, the specimen being heated to the required temperature and rapidly bent through a predetermined angle, usually 90° or 180° , malleability at temperature being assessed by the extent to which cracking occurs. Forging and bend tests may be used together, as described in recent work on nickel and nickel alloys by Martin and Bieber,¹⁰ who claim, as a result of extensive experience in the interpretation of hot bend and forging tests under standard conditions, that the behaviour on hot rolling can be predicted with considerable accuracy.

Thrig^{11, 12} and Clark and Russ¹³ have applied torsion tests for evaluating the capacity of material to hot pierce satisfactorily, the value taken as the index figure being the number of twists needed to produce fracture in rod samples at the testing temperature, and measurements of the torque required to effect twisting have been used as an indication of the power requirements in piercing. This method has been employed to determine the effect of impurities upon the hot workability of steel, and also to control hot piercing of steel in the mill, but does not appear to have been used much in connection with non-ferrous materials.

Forging or flattening tests are extensively used in assessing hot workability, since they can be easily and quickly carried out, and, as distinct from some other types of test which have been briefly referred to which measure some property that needs to be interpreted into a measure of workability at elevated temperature, forging or flattening tests, like rolling and extrusion on a small scale, provide much more direct and useful evidence. A simple but very useful and informative test is the bar forging test, illustrated in Fig. 1 (Plate LXXI), in which a specimen of 1-in.-dia. extruded rod is forged down progressively to a relatively thin edge. The test can be carried out with several preheatings if it is desired to maintain the forging temperature between defined limits, or it may be continued down to comparatively low temperatures to assess hot-working properties over a wide temperature range. This test, like the other forging and flattening tests mentioned below, is extremely useful in evaluating forging and stamping qualities, for they approximate to actual working conditions and can be carried out on samples of the material to be processed. That is, they can be, and, in fact, are, used

as acceptance tests (B.S. No. 218, 1940) and not only in exploratory or investigational work. In such a flattening test specimens of standard dimensions cut from rod are depressed to a predetermined extent or dealt a blow of constant energy, over a range of temperature, and the extent of deformation and freedom or otherwise from edge cracking afford a reliable indication of their forging or stamping characteristics. An example of the test is illustrated in Fig. 2 (Plate LXXII), which reveals the effect of lead in decreasing the temperature range over which a 60 : 40 brass alloy can be satisfactorily hot stamped. In this test the specimen cylinders, 1 in. in both height and dia., cut from extruded rods, were reduced in one blow to a thickness of 0.2 in. at various temperatures. Hot shortness manifests itself by rough or crumbly cracking at the disc edge, and, when it is severe, on the flat surfaces too, but when edge cracking results from forging or stamping at too low a temperature, the cracks are sharper and smoother and quite different in appearance from the hot cracks at the other end of the temperature range.

V.—THE EFFECT OF COMPOSITION ON THE HOT WORKABILITY OF COPPER AND COPPER ALLOYS.

1. *Copper.*

The many types and varieties of copper available industrially are without exception readily hot workable between 800° and 900° C., in which temperature range the low resistance of the metal to deformation enables such operations as rolling, extrusion, and forging to be carried out with considerable latitude in working conditions and little risk of cracking, fracturing, or other kind of failure.

The greatest proportion of high-grade copper, that is, copper of low impurity content, is now made and used in the tough-pitch form, that is, high-conductivity copper, with smaller amounts of high-conductivity oxygen-free copper and phosphorus-deoxidized copper, all three of which have good hot-working properties over a very much wider range of temperatures than the less pure grades, in which traces of such elements as bismuth restrict the hot-working range and generally increase the difficulty and reduce the scope of any hot-working process.

The oxygen content necessary to obtain the condition, characterized by the level set surface of the ingot, which is associated with toughness, increases with the impurity content of the metal. Thus in the highest grade of copper the oxygen content is invariably low (generally between about 0.015 and 0.04%), and this amount of oxygen has no apparent effect on rolling or extrusion over a wide range of temperatures. Indeed,

it is not uncommon to begin the hot rolling of high-conductivity copper slabs for strip and sheet at temperatures between 650° and 750° C., the diminished oxidation at this temperature of preheating resulting in a marked improvement in the surface quality of the final cold-rolled product as compared with that of material hot rolled between 800° and 900° C. The good hot-working qualities of H.C. copper are well illustrated by wire-rolling practice, in which horizontally or vertically cast bars of some 4×4 in. cross-section are hot rolled from about 850° C. in a continuous series of operations without intermediate reheating to a final dia. of $\frac{5}{16}$ – $\frac{1}{4}$ in. For such operations, however, as rotary piercing, oxygen-bearing coppers are less suitable than varieties free from oxygen.

Coppers not containing oxygen include oxygen-free high-conductivity and deoxidized varieties of otherwise high-purity copper, in which residual phosphorus is generally present in amounts ranging from 0.005 to 0.05%. The most usual method of making deoxidized coppers is to add an excess of phosphorus to an oxygen-bearing copper. Some excess of phosphorus is inevitable in such a procedure, and is, indeed, essential to take care of possible oxygen pick-up in pouring. Very high ductility and outstanding workability over a wide range of temperatures are claimed for oxygen-free high-conductivity copper made by the charcoal reduction of an H.C. grade of copper, followed by pouring out of contact with air, and this material may be alloyed with 0.005–0.015% phosphorus before pouring. It would appear that as far as the slight differences in hot-working characteristics of these different grades of copper can be assessed, the advantage may, in certain circumstances, lie with a low-phosphorus rather than an oxygen-free copper.

The raw copper used in making arsenical grades is generally less pure than H.C. copper, and the oxygen necessary to maintain the pitch is correspondingly higher. Arsenical coppers contain usually 0.3–0.5% arsenic, which amount has a marked effect on the hot-working properties, for, apart from increased resistance to deformation, the tough-pitch varieties are hot short between 600° and 700° C. The hot working of these coppers is begun between 800° and 900° C., within which range rolling is readily effected and with careful manipulation may be continued well into the range in which the cast alloy is brittle. Brittleness is most pronounced with a low arsenic and high oxygen content, the most difficult materials to hot work being those with about 0.05% arsenic, especially when the oxygen exceeds about 0.05%. In phosphorus-deoxidized arsenical coppers, on the other hand, the brittle range is entirely absent and hot working is possible at all temperatures up to 900° C., although ductility is generally not so good as in the deoxidized H.C. coppers already referred to.

Other alloying additions made to copper to achieve some improved property with the minimum adverse effect on conductivity include silver, cadmium, chromium, and tellurium. Silver is added to H.C. coppers in amounts up to about 0.05% and has no appreciable effect on hot rolling. Cadmium copper is generally produced as wire, and the alloy containing 1% cadmium, provided a proper melting procedure has been used, is completely deoxidized and can be readily hot rolled by a process comparable with that used for H.C. copper wire, the main difference being that rolling is slowed down and the temperature deliberately allowed to fall, with the object of securing a measure of cold working at quite an early stage, thus increasing the hardness and strength of the final cold-drawn product, but the alloy can equally well be rolled at the higher temperatures normally used for copper wire. The hot rolling of copper containing chromium additions of up to about 1% is normally maintained at temperatures in excess of about 700° C. to avoid temperature ranges below this, where age-hardening effects may occur. In making free-turning copper, tellurium to the extent of about 0.75% is added to remelted cathode copper, without the use of any deoxidant, but oxygen-free conditions are maintained throughout the alloying and pouring process. This amount of tellurium has less effect on the hot workability of high-grade copper than the much smaller amounts present in some less pure coppers, for the alloy can, in fact, be extruded and hot rolled without particular difficulty.

Early work ^{14, 15} on the hot rolling of copper showed that sulphur in much larger amounts than are ever present in commercial coppers is without effect on the hot-working properties. Sulphur has, however, an indirect effect associated with the reactions involved in the fire-refining process. Sulphur is present in the crude copper and is removed by oxidation in refining, although further sulphur contamination can arise from the use of unsuitable fuels in the refining furnace. The presence of sulphur means that a satisfactory pitch can be attained only with an unduly high oxygen content, and this, particularly if arsenic is also present, restricts the hot-working range.

In the earlier days of fire-refining, when many of the raw materials were less pure than those now available, additions of lead were made to copper to assist in controlling the pitch, but nowadays this practice has been discontinued. The investigations of Archbutt and Prytherch ¹⁶ have shown that up to 0.5% lead may be present in tough-pitch copper without seriously affecting the hot-rolling properties or the electrical conductivity of the product. With lower oxygen contents the lead tolerance is correspondingly reduced, and in deoxidized copper the permissible lead content is generally considered to be about 0.02%,

although quantities of this order are seldom met with, since no raw coppers contain these amounts of lead.

The adverse effect of bismuth on hot workability is most pronounced in the lower temperature ranges of working, i.e. below 750°C ., where, because of reduced solubility, the element or one of its compounds separates on the grain boundaries where the metal breaks down under the stresses occurring in hot working. As far as investigations on a plant scale of operation are concerned, the largest amounts of bismuth on which information is available are 0.006% in tough-pitch¹⁷ and 0.010% in deoxidized copper,¹⁸ neither of which appears adversely to affect hot working in the temperature range 800° – 900°C ., where the element is probably in solid solution. At lower working temperatures the permissible limits are smaller, and in deoxidized copper as little as 0.002%^{4, 18} may be deleterious, but in an oxygen-bearing copper some of the bismuth is present in the oxide phase and hence the tolerance is somewhat increased. According to earlier investigations¹⁶ the deleterious effect of bismuth on hot workability was less marked in the presence of arsenic, but more recent investigations^{4, 18, 19, 20} have not shown any important differences between the behaviour of arsenical and non-arsenical coppers in this respect.

Selenium and tellurium occur as impurities in some grades of fire-refined copper and are often associated with bismuth. In the absence of bismuth, up to about 0.05% selenium or tellurium or of the two together can be present without affecting the hot-working properties in the range 800° – 900°C . When as little as 0.003% bismuth is present, however, hot working is rendered impossible by the presence of more than 0.025% tellurium or selenium, the former element being rather more deleterious than the latter.^{19, 20} Hot working of alloys with selenium and tellurium in the lower temperature ranges has not been systematically investigated, but the adverse effect of both elements is undoubtedly greater at temperatures below about 750°C .

2. Copper-Zinc Alloys.

Industrial binary copper-zinc alloys range in copper content from 54 to 97% and differ considerably in structure and properties and in hot-working characteristics. In the equilibrium condition alloys containing 54–56% copper consist wholly of the β phase, those with copper contents of 56–62% are duplex $\alpha + \beta$ alloys, while those with 62% and more are entirely α .

Morris²¹ has shown that throughout the α range of alloys containing 90–65% copper the changes in resistance to deformation at elevated temperatures with copper content are small, and in industrial practice

no difference is made between the sequence of rolling passes for gilding metal and that for a 65 : 35 brass, for example, although the temperature at which rolling commences is usually higher with the higher-copper alloy. Although, as already noted, the hot working of α alloys is being increasingly adopted in the manufacture of strip, sheet, tube, rod, and section, successful production calls for a close control of purity levels and quality of ingot or billet. While it is true that in an otherwise pure copper-zinc alloy the addition of, say, 1 or 2% of such elements as nickel, aluminium, or tin, has no marked effect on hot workability in general, the simultaneous presence of very much smaller amounts of several impurities can be extremely detrimental, but little detailed information of this matter has so far been published. Of the elements which may be added to α copper-zinc alloys for various reasons, none, other than lead, seems to affect hot workability in the amounts in which it would normally be present. Thus, such alloys as Admiralty brass and aluminium brass can be hot rolled and extruded, for example, under much the same conditions as 70 : 30 brass, and, like 70 : 30 brass, need the same careful control of purity, casting, and processing conditions.

Lead is extremely deleterious to the hot-working properties of α brasses, and various investigators ^{22, 23, 24} have reported that as little as 0.01% lead in 70 : 30 brass causes cracking in hot rolling. Experience indicates, however, that with proper control of casting conditions and careful preheating to within narrow temperature limits, the maximum permissible lead content for hot rolling is about 0.025% and for extrusion 0.05%, although normally lower figures are worked to, so as to realize a greater working margin in operating conditions.

In amounts of the order of about 0.05%, arsenic or antimony is added to increase resistance to dezincification and does not impair the hot-working properties. McLean and Northcott ²⁴ have shown that cracking on hot rolling occurs if the antimony content exceeds 0.075%, whilst in the presence of 0.01% lead the maximum permissible antimony content is 0.04%. Bismuth in amounts as small as 0.005% has a very adverse effect on the hot-rolling properties of α brasses.

The straight copper-zinc alloys within the $\alpha + \beta$ and β fields are amongst the most easily hot workable of all the copper alloys. Although some of the duplex alloys are produced as hot-rolled plate and sheet, most of the production, and practically all of that of the β alloys, is in the form of extrusions. Alloys containing about 58–60% copper can be hot worked readily in the range 600°–850° C., but as the copper content is decreased the upper limit is reduced, and at 56% copper it is about 750° C. Brasses of these types, however, usually contain additions of one or more of such elements as lead, tin, silicon, nickel, iron, aluminium,

and manganese, which have no adverse effect in extrusion, except, in some instances, to increase the working pressures required. In rolling and forging the same is substantially true; that is, the presence of these elements does not narrow the hot-working range, although the resistance to deformation may be increased. Lead, however, is an exception, for it has a pronounced effect in inducing hot shortness.

The effect of increasing amounts of lead on the extent to which edge cracking occurs during the hot rolling of an otherwise pure 60 : 40 brass is illustrated in Fig. 3 (Plate LXXIII). In the absence of lead, the edges are free from cracking, but with an increase in lead content to 1% the cracking is appreciable. The same figure illustrates the crack-free condition of the edges of hot rolled 60 : 40 brass containing 1% iron, and a comparison of the middle photograph with the last shows the improving effect on hot workability, as evidenced by decreased edge cracking in hot rolling, of the presence of iron in an alloy containing lead. The embrittling effect of lead at elevated temperatures is also clearly demonstrated by hot flattening tests. In the absence of lead, cylinders of equivalent height and dia. of the pure $\alpha + \beta$ type of alloy can be depressed in one blow to one-fifth of the original height without any edge cracking at temperatures ranging from 600° to 850° C. With 1.5% lead, the crack-free range under the same conditions is reduced to 650°–800° C., while with 3% lead it is limited to temperatures between 700° and 750° C., as shown in Fig. 2 (Plate LXXII). Similar tests show that additions of iron and aluminium offset the embrittling effect of lead. Some of the specially alloyed brasses, not containing lead additions, have notably good hot-working properties, as exemplified by the type of high-tensile brass containing, nominally, 1% iron, 2% manganese, and 3% aluminium, cylinders of which can be flattened in this test without edge cracking at temperatures ranging from 600° to 850° C.

As to the influence of other elements, little detailed or systematic information is available, though 0.01% bismuth does not appear to bring about any embrittlement in hot-rolling brasses of the 60 : 40 type, while selenium and tellurium in similarly small amounts seem to be without any adverse effect in extrusion and stamping, and Rae²⁵ has reported that up to 0.02% antimony is not detrimental so far as hot workability is concerned.

3. Nickel-Containing Alloys.

All the alloys of the cupro-nickel type, which mostly range in nickel content from about 10 to 30%, and are produced mainly in the form of strip, tube, sheet, and plate, can be readily fabricated by hot rolling or extrusion, although temperature limits to avoid cracking in hot rolling

are somewhat critical. Purity is important, however, especially as regards such elements as oxygen, sulphur, carbon, and lead. Other elements such as iron, manganese, and chromium are not infrequently added, and sometimes aluminium, for special purposes, but they do not impair hot workability. The careful use of deoxidants such as manganese and magnesium, which are also valuable in counteracting the effect of any sulphur which might be present, and precautions to avoid carbon contamination in melting are important if the maximum capacity for both hot and cold working in this inherently very ductile series of alloys is to be fully realized.

Ternary copper-nickel-zinc alloys produced in wrought forms fall into one of two classes: the single-phase α alloys, known as the nickel silvers, and the duplex $\alpha + \beta$ or β alloys, which are referred to as the nickel brasses. The α alloys mostly come within the range 10–30% nickel and 58–65% copper, and are stronger and less ductile at high temperatures than the α brasses, thus requiring more power for hot working, or, alternatively, a higher working temperature. They are at least as sensitive as the α brasses and the cupro-nickels to the effect of impurities, especially in hot rolling, which is usually commenced at about 900° C. Conditions for satisfactory hot rolling, which vary with different basic compositions, are critical. Little information has so far been published concerning the effect of specific impurities on the hot workability of these alloys, but in material for hot rolling the lead content should be kept below 0.02% and the ingot should be cast under conditions producing a fine grain structure. Although manufactured mostly in the form of sheet and strip, the α alloys can also be made in extruded forms.

The nickel brasses, that is, alloys containing 6–18% nickel and 38–45% zinc, include structurally $\alpha + \beta$ and β alloys, which, like the corresponding copper-zinc alloys, can be hot worked over a wide range of temperature in extrusion, forging, or hot stamping.²⁶ The alloy containing 45% each of copper and zinc has very good hot-working properties, but with increasing nickel content the alloys become less readily extrudable. Although lead does not adversely affect extrudability, it seriously impairs the hot-stamping or forging behaviour. There is also evidence to show that appreciable amounts of silicon or manganese have no adverse effect on either extrusion or stamping properties, which are impaired, however, by the presence of phosphorus.

4. Aluminium Bronzes.

The alloys of copper and aluminium are, like the brasses, produced commercially in both the α and $\alpha + \beta$ ranges of composition, and both

types of alloys can be, and are, produced by hot-working operations. Again, like the brasses, the α alloys are not so easily hot workable as the $\alpha + \beta$ alloys, but provided impurities such as lead and bismuth are avoided, no serious difficulties or problems present themselves in hot working. These materials, as well as α alloys with additions of such elements as manganese, nickel, and iron, are being hot rolled to an increasing extent in the manufacture of plate, sheet, and strip, and are also regularly produced in the form of tube shells by extrusion.

The β phase of the copper-aluminium series has a similar crystal configuration to that of the β phase in the copper-zinc series, and the alloys have correspondingly good hot-working properties. Binary alloys with aluminium contents of the order of 9–11% can be hot rolled, extruded, and forged without difficulty, and there is no evidence of any hot-short range, the material being workable from 950° C. downwards. Alloys in this range of aluminium content usually carry other alloying elements, especially nickel, manganese, and iron—often all three—and sometimes lead and zinc. Although the three first do not adversely affect hot workability, by causing hot shortness for example, they progressively reduce plasticity and, therefore, necessitate the use of high working temperatures or pressures. Zinc in the amounts in which it is likely to be added to alloys of this type has no adverse effect, but the presence of lead, on the other hand, causes cracking on hot rolling and largely restricts hot working to extrusion, although such extruded stock can be subsequently hot forged.

5. *Silicon Bronzes.*

The silicon bronzes produced in wrought form usually contain up to 3% silicon with additions of up to 1% manganese, tin, or zinc. They are single-phase alloys, ductile at room temperature and, in consequence, can be readily cold worked, but they are equally suitable for hot working by rolling, extrusion, and forging. Processing into plate, sheet, rod, section, and tubing is usually begun in the temperature range 850°–900° C., and while there is no evidence of hot shortness at lower temperatures, as the loads and pressures needed for deformation are relatively high, working is generally carried out towards the upper limit of the ductile range. Although small amounts of such elements as iron and nickel do not seem to have any untoward effect on hot workability, other impurities such as lead need to be restricted to less than about 0.05% if successful hot working is not to be limited to extrusion, which is generally the case if more lead than this is deliberately added to improve machinability.



FIG. 1.—Hot-Forging Test on Brass Rod.



60 : 40 brass + 3% lead.
 60 : 40 brass + 1 1/4% lead.
 FIG. 2.—Effect of Lead in Hot-Flattening Tests.
 Stamping temperatures (top to bottom) : 850°, 800°, 750°, 700°, 650°, 600° C.

60 : 40 brass.

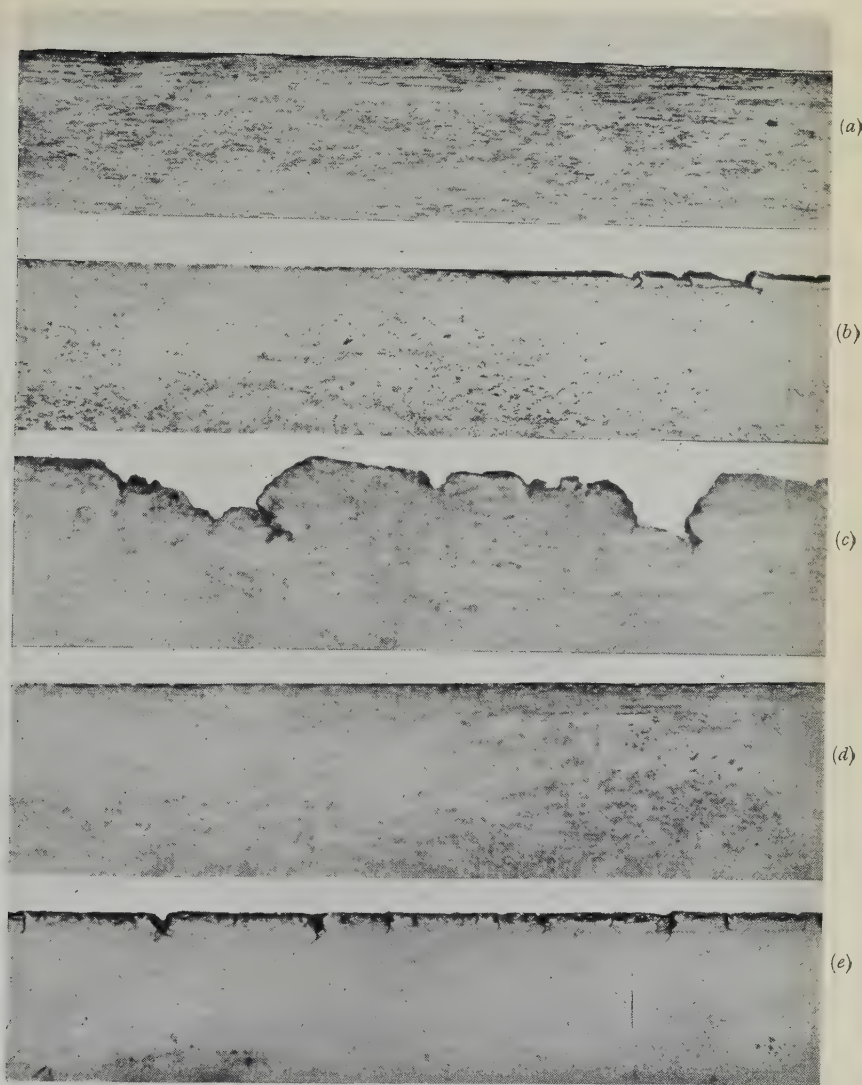


FIG. 3.—Effect of Lead and Iron on Edge Cracking of 60 : 40 Brass Strip in Hot Rolling.

- (a) 60 : 40 brass.
- (b) 60 : 40 brass + 0.3% lead.
- (c) 60 : 40 brass + 1.0% lead.
- (d) 60 : 40 brass + 1% iron.
- (e) 60 : 40 brass + 1% lead + 1% iron.

STRUCTURES OF EXTRUDED BRASS ROD.

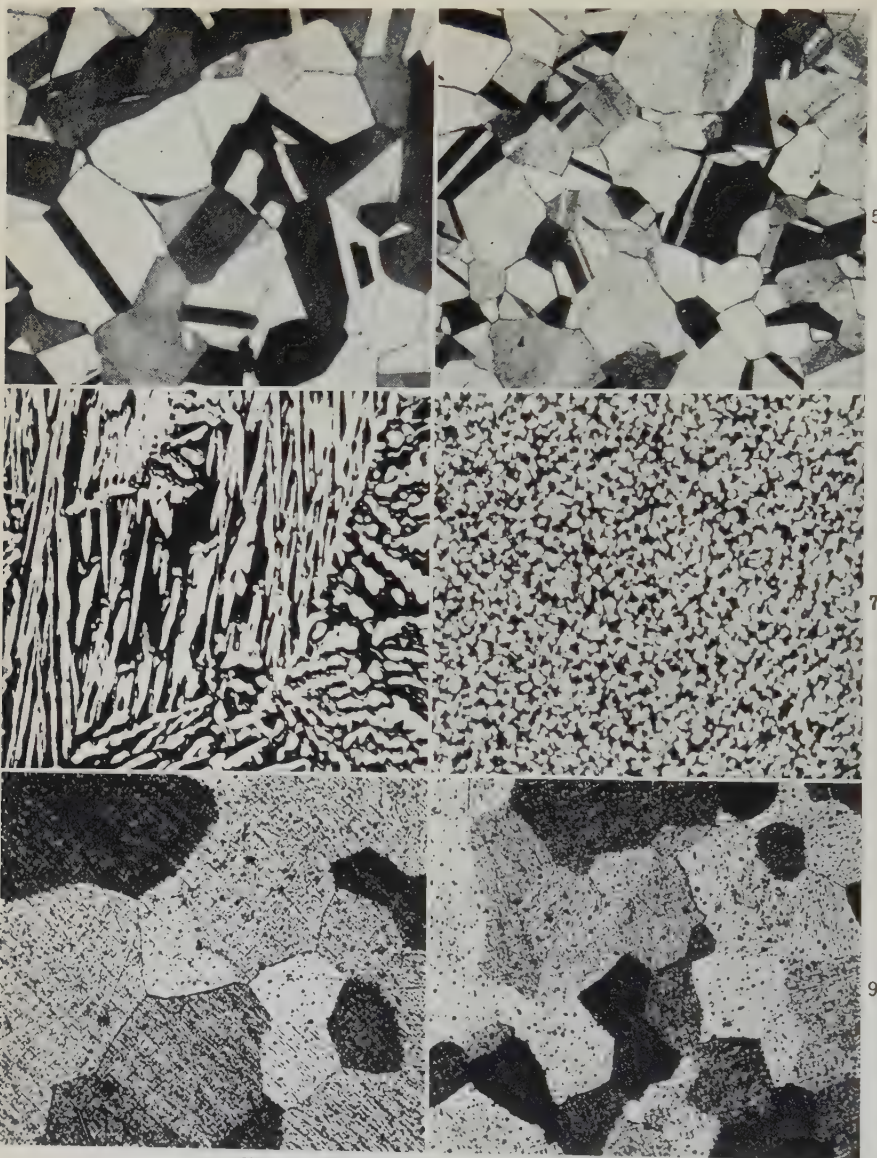


FIG. 4.—Front end, 70 : 30 brass.

FIG. 5.—Back end, 70 : 30 brass.

FIG. 6.—Front end, 60 : 40 brass.

FIG. 7.—Back end, 60 : 40 brass.

FIG. 8.—Front end, β high-tensile brass.

FIG. 9.—Back end, β high-tensile brass.

All $\times 100$.

VI.—HOT-WORKING PROCESSES.

1. *Hot Rolling.*

Copper of various grades and qualities and some copper alloys, such as 60 : 40 brass, Naval brass, silicon bronze, and cupro-nickel, are produced as plates in large quantities by hot rolling to the finished gauge, the only cold-working operation being flattening and shearing. Ingot sizes, varying according to the size of plate required, range up to 10 in. thick, and may be as much as 5 ft. square, weights of 5 tons being not uncommon. Mechanical handling is, therefore, essential, and ingots are fed into and withdrawn from the reheating furnace by charging machines, whilst live carrier rolls take the ingot to the mill. The roll stands are usually of the two-high reversing type, with chilled- or grain-iron rolls, and it is not general practice to have edging rolls fitted.

Hot rolling is usually begun at the highest practicable temperature for each alloy, in order to obtain maximum reductions between the reheating operations, which are generally necessary in plate manufacture. Thus, the various coppers are preheated to about 900° C., the brasses and silicon bronzes to 850° C., and the aluminium bronzes and cupro-nickels to 900°–950° C. In the early stages of production, rolling is continued only as long as the temperature of the slab remains sufficiently high for economically large reductions to be made, but as the plate approaches the finished size maintenance of temperature is more difficult and rolling at this stage is not unusually continued to red heat if the properties of the material being rolled permit. Cross rolling to increase the width is usually essential, and the stage at which this is effected depends largely upon the width of the plate required and the facilities of the mill, particularly with respect to the width of the initial breaking-down rolls.

Most of these materials produced as plate can be hot rolled without difficulty, and except in unusual instances, occasioned perhaps by some abnormality in composition or treatment, the incidence of edge or surface cracking is negligible. It is usual to overhaul the surface, and this is done either on the ingot or the partially rolled stock or both. Copper plates are generally descaled by reheating and quenching in water, while alloy plates are acid pickled.

Copper and some copper alloys, more usually those of the 60 : 40 brass type, are produced in the form of hot-rolled sheet, that is, hot rolled to finished dimensions, but this practice is becoming less common and giving place to cold finishing of hot-broken-down stock on modern wide strip mills. Hot-rolled sheets are produced by further rolling of blanks sheared from hot-rolled plate, but more usually by hot rolling

small ingots of a size which permits of manual handling throughout. Copper wedge cakes, for example, from 100 to 250 lb. in weight, and alloy ingots of comparable size, are hot rolled on two-high non-reversing mills, with chilled-iron rolls, the stock being passed through the rolls and returned manually over the top roll. In the production of thin sheet, pack rolling, that is, the rolling of two or more sheets together, is carried out.

For the hot rolling of rod and section, either to finished sizes or as a preliminary breaking-down for subsequent cold processing, three-high section mills, equipped with chilled- or alloy-iron rolls, are commonly employed. The sequence of passes used in the breaking-down stages of rod rolling is varied for different alloys, since because of differences in plasticity at working temperatures, the extent to which the grooves are filled varies, and for easily deformed alloys over-filling of the grooves may occur, which subsequently causes laps or spills to form on the stock. All pass sequences, however, are basically designed to afford the necessary working at the centre of the billet, and involve alternate square and rectangular sections in the earlier breaking-down, and oval, square, and circular grooves in the finishing train. In wire-rod rolling, after suitable breaking-down, some form of continuous mill may be used, the Belgian or loop wire mill being not uncommon, to provide stock at some convenient size for subsequent cold drawing. This method of manufacture of wire-rod stock is very commonly used in the production of H.C. copper by rolling square-section wire bars of 130–540 lb. in weight, whilst for the copper alloys round billets are more usually employed.

It is in strip rolling, however, that improvements in hot breaking-down have made most progress recently, and in the production of copper and many copper alloys in strip form hot breaking-down is now extensively employed. The ingots used range in weight from 600 to 2000 lb. or more and are not uncommonly preheated in furnaces controlled in respect both of temperature and atmosphere. Rolling units are of the two-high reversing or three-high type, and the ingots are mechanically extracted from the reheating furnace and fed to the working rolls by driven carrier-table rolls, and the three-high mills are fitted with hydraulically or electrically operated lifting tables. Auxiliary equipment on the mill stand itself may include guides, edging rolls, water sprays, &c., whilst at the end of the run-out tables arrangements may be made either for hot coiling of the stock or hot shearing, depending upon the nature of the subsequent finishing operations. In one preheating the material is rapidly rolled down on such mills from an initial ingot thickness of several inches to thicknesses usually of the order of $\frac{1}{8}$ – $\frac{5}{8}$ in.,

according to particular circumstances and requirements. Because of the high quality of surface finish required on the final product, hot breaking-down is usually followed by surface overhauling. To reduce the extent to which surface treatment of the stock is required, it is essential to maintain the roll surface in good condition, and the provision of automatic grinding blocks actually applied to the roll surface whilst working is not uncommon.

2. *Extrusion.*

The advent of extrusion as a hot-working process in the wrought copper alloy industry dates back just over fifty years, and now very large tonnages of a wide range of materials are produced in this way in the form of rod, section, tubes, shells, &c. The bulk of this tonnage is made up of brass alloys of one sort or another with copper contents in the range 55–65%, for they are, in the main, very easily extrudable. In lesser quantities other alloys such as the cupro-nickels, tin bronzes, aluminium bronzes, nickel silvers, and silicon bronzes are also produced in extruded forms.

Essentially, the process consists of forcing plastic metal at a suitable temperature through a shaped orifice in a metal plate known as the die. Two methods of working the extrusion process have been developed, the direct and indirect, which differ in respect of the relative movement of container and metal to be extruded. In the direct process the pressure necessary for extrusion is applied to a ram located at the opposite end of the container from the die, towards which it moves, pushing the metal in front of it and so through the die. In the indirect process, on the other hand, the die is forced into the metal, usually by a hollow ram, through which the extruded product passes, there being no relative movement of container and metal. The direct process is used almost exclusively and is generally more easily and conveniently manipulated, particularly when multi-hole dies are being employed.

Both horizontal and vertical types of press are in commercial use, and whilst rod and section are invariably extruded on horizontal presses, either may be employed for the extrusion of tubes, the selection depending largely upon the dimensions of the finished product. For the manufacture of condenser tubes and the like, the vertical press with its rapid action and high degree of concentricity of piercing is generally preferred. Recent advances in the design of horizontal presses, however, have served to overcome to a large extent the original defects of this type for tube production, and when press capacity in excess of about 1500 tons is required the horizontal press is generally regarded as the more suitable. Press capacities range up to 7500 tons and container

dia. up to 10 in., but by far the greatest tonnage of copper-base alloys is produced on presses with containers 8 in. in dia. or less, with capacities of not more than 2500 tons.

The dies employed in these extrusion processes have to withstand high stresses at elevated temperatures, and also the wear involved in the passage of hot metal through the orifices. The number of types of steel suitable for such service is limited, and one which is widely used is that carrying between 8 and 10% tungsten, used after oil hardening and tempering to a Brinell hardness of 350–450. Contact of the die with the hot metal results in loss of hardness and in closing up of the die contour, which necessitates servicing in the form of opening out and re-heat-treating. Mandrels in tube extrusion are subjected to even more onerous conditions than those for extrusion dies, and are made from 8–10% tungsten, 2.5% nickel steels in the hardened and tempered condition. Increased life is secured by adequate cooling and lubrication of the mandrel, and these are effected at one and the same time by quenching the mandrel in a suspension of graphite in oil after each extrusion cycle.

The extrusion process has been the subject of considerable investigation during the past forty years,^{27, 28} and the effects of various factors upon the pressure required for extrusion are now well established and the mechanism of flow has been examined by a number of workers.^{29, 30, 31} Temperature has the most marked influence upon the extrusion pressure, an increase in temperature reducing the pressure required, but the speed of extrusion within the limits normally encountered has, in itself, little effect upon pressure, unless, of course, it is associated with marked cooling, which would cause the extrusion pressure to rise. The higher the extrusion ratio, which is defined as the ratio of area of billet to area of rod, the higher is the pressure required, and thus for smaller-dia. rod or section of small area multi-hole dies are employed, in which die shape and disposition of the various holes is a matter for careful consideration.

Studies of the mechanism of metal flow during extrusion^{29, 30} have explained the cause of defects which may occur at the back end of extruded rods and how such defects can be avoided. The most important of the precautions to be taken is the use of pressure discs of slightly smaller dia. than the container, so that a skull containing the exterior surfaces of the billet is left in the container after extrusion. Another method particularly used in tube manufacture is to machine the billets before extrusion and preheat in controlled-atmosphere furnaces to minimize oxidation.

An indication of the initial temperature used in the extrusion of copper and copper alloys is given in Table II (p. 508). Unless the con-

tainer is heated, and it is quite common for it not to be, the temperature can fall appreciably during the extrusion cycle, the duration of which is one of the chief factors in determining the extent of the differences in structure, properties, and dimensions between the front and back end of the rod. In general, with metals or single-phase alloys, either all α or all β , the grain-size of the front end is larger than that of the back end, whilst the grain structure at the front end of an extruded $\alpha + \beta$ brass is coarser than that of the last portion to be extruded. Figs. 4-9 (Plate LXXIV) provide an indication of the kind of structural variations which can occur. They relate to $\frac{3}{4}$ -in.-dia. rods extruded through a single-hole die into lengths of about 56 ft. from 5-in.-dia. billets in 70 : 30, 60 : 40, and a β high-tensile brass, the last being the alloy referred to in the third section of Table III. These structural differences are reflected, more especially, of course, in the $\alpha + \beta$ type of alloys, in the physical and mechanical properties of the rod, examples of which are given in Table III for rods extruded through a single-hole die from 5-in.-dia. billets. In the course of extrusion a number of factors operate which affect the dimensions of the product, the net effect resulting in a somewhat larger dia. at the back end than at the front end of the rod, as illustrated by the values given in Table III. The properties of extruded rods are also affected by the amount of deformation which has taken place in extrusion, but, as in most extrusion operations, the reduction in area from billet to rod is 90% or more and the difference in mechanical properties between large- and small-dia. rods is not very marked. The values quoted in Table III show the influence of rod size upon mechanical properties for each of three alloys over a range of reduction of areas by extrusion, from 90.5 to 96.5%.

3. *Rotary Piercing.*

As a first hot-processing operation in the manufacture of tubing, shells are made by rotary piercing of solid billets as well as by the extrusion of solid billets or cast hollow shells. In the mills now used for rotary piercing the hot billet is spun between two heavy barrel-shaped rolls or bevelled discs, the axes of which are inclined at an angle to each other and to the axis of the billet. Since the rolls or discs rotate in the same direction, an advancing movement is created, which draws the spinning billet between them. The compression to which it is then subjected results in a radial tensile stress at right angles to the direction of the compressive force, and this tends to open the billet axially. These radial tensile stresses change direction as the billet rotates, leading to the formation of a central cavity which is smoothed into a circular hole by the plug. It is the incidence of these stresses set up in the interior of the

TABLE III.—*Properties of Extruded Brass Rods.*

Composition						Rod Dia., in.		Position of Test *	Limit of Proportionality, tons/in. ²	0.1% Proof Stress, tons/in. ²	Tensile Strength, tons/in. ²	Elongation, % on 4√L	D.P.N. (10 kg.)
Copper, %	Iron, %	Manganese, %	Aluminum, %	Tin, %	Lead, %	Nominal	Actual						
60.15	0.03	0.02	Nil	0.03	0.48	1.5	1.559 1.560	F B	6.7 11.0	10.0 11.8	27.0 29.5	48.5 43.5	96 102
59.94	0.07	0.01	Nil	0.05	0.47	1.0	1.066 1.070	F B	7.5 10.8	10.2 12.4	28.6 30.7	44.5 37.5	114 122
59.93	0.03	0.02	Nil	0.03	0.70	0.75	0.812 0.813	F B	7.8 11.6	14.2 14.2	28.9 30.9	50.0 43.0	95 120
56.73	0.95	1.55	0.05	1.16	1.73	1.5	1.560 1.563	F B	8.6 9.3	12.8 14.5	32.3 34.4	33.5 26.5	125 146
56.85	0.96	1.34	0.1	1.29	1.64	1.0	1.068 1.069	F B	9.2 10.6	13.0 15.0	33.5 35.4	37.0 23.0	124 130
57.16	1.06	1.65	0.03	1.15	1.58	0.75	0.812 0.814	F B	9.4 9.4	12.6 14.1	34.4 35.6	35.0 24.0	122 132
56.34	1.04	2.33	1.88	0.03	0.02	1.5	1.561 1.563	F B	13.0 13.3	18.1 18.7	43.5 45.2	23.5 23.0	179 193
56.29	1.01	2.38	1.87	0.02	0.02	1.0	1.068 1.069	F B	14.4 14.48	19.5 20.2	45.0 46.3	23.0 23.0	180 194
56.27	1.09	2.33	1.82	0.03	0.02	0.75	0.814 0.817	F B	14.4 14.8	19.2 19.3	46.0 48.0	23.0 23.5	186 194

* F = Front End, B = Back End.

billet and the consequent severe and rapid deformation which make tube piercing such a searching hot-working operation, necessitating the highest quality of material and castings.

Because of its high rate of production and the time involved in changing roll and plug settings for different shell sizes or different materials, rotary piercing is much more suited for bulk than for intermittent and varied production. It is used extensively, and most generally, in making copper shells and only to a much lesser extent for tube shells in other copper alloys, such as gilding metal, α , and $\alpha + \beta$ brasses. In the production of copper shells for subsequent cold drawing, cast billets, usually about 3-8 in. in dia., are used, with the lower sizes predominating, much of the output being from 3-4-in. billets of 100-200 lb. in weight.

Little work has been published on the fundamental characteristics of the piercing operation, and that which is available relates to steel, for which some of the relationships between roll and plug sizes and their effect upon the mechanism of flow have been worked out.³²

4. Forging and Stamping.

The hot stamping of copper and its alloys, by single or repeated blows, using open or closed dies, is variously described as forging, pressing, or stamping. The products are usually, and relatively, small in weight, the bulk of the tonnage being in the form of hot stampings, produced from slugs cut from extruded stock, heated to the required temperature, withdrawn from the furnace, and struck between dies. In hot stamping, or press forging as it is otherwise termed, the shaping is effected in a single blow in a press actuated mechanically by crank or screw, or hydraulically. The dies are usually split along some convenient centre line, one half being fixed, and the other in the moving platen of the press.

In drop forging also one half of the mating die is in the hammer, the other in the anvil, but the metal is subjected to repeated blows to produce the finished form. Upset forging, as its name implies, is usually employed in the production of such articles as headed bolts from rod stock, where some form of mechanical press is used, with dies moving in the horizontal plane in contrast to the more usual vertical movement in press forging.

The metallurgical issues involved in stamping and forging concern effective temperature control, appropriate to the materials being forged, the selection and treatment of suitable die materials, and the important matter of die design, all of which require individual consideration.

Although many copper alloys, especially those of the $\alpha + \beta$ and β types, can be readily hot forged or stamped, those most generally used are the brasses. As previously noted, those alloys of this series with the greatest capacity for hot working in this way are the straight alloys of the 60 : 40 type, but to facilitate subsequent machining lead additions of the order of 1.5% are very commonly made. High-tensile brasses are also produced in the form of forgings and stampings, as well as Naval brass, nickel silvers, aluminium bronzes, and, usually for electrical purposes, pure copper.

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THE HOT WORKING OF TIN BRONZES.* 1230

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SYNOPSIS.

An attempt has been made to examine the influence of various factors on the hot-working properties of phosphorized tin bronzes. The use of pure materials is thought to be essential, because of the tendency of low-melting-point impurities, such as bismuth, lead, and antimony, to segregate inversely in the grain boundaries. The harmful effects both of these impurities and of tin sweat can be reduced by controlled melting and pouring. In assessing the influence of the tin and phosphorus contents of the bronze on its hot-working capacity, previous work, mostly on a laboratory scale, is discussed, and the difference between working on a material at elevated temperatures and hot working the material on a commercial scale economically is emphasized. It appears that bronzes are intrinsically harder to hot work than most copper-base alloys, and must be worked within a narrower temperature range; the true reason for the latter is not yet fully understood. There is a brief discussion of the hot rolling and extruding of bronzes, with descriptions of successful methods of working phosphorized bronzes containing up to 10–15% tin.

I.—INTRODUCTION.

UNTIL comparatively recently, it was assumed that the phosphorus-tin bronzes were almost unworkable in the hot state, or that only the lower-tin bronzes could be worked hot at all. This state of affairs is reflected in the very small amount of published work on this subject. It is not until the late 1920's that any reference of importance is made to the hot working of bronze, and then most of the papers published deal with experiments on a laboratory scale, as, for example, the work by Bauer and Vollenbruck¹ on the hot forging of 20% tin bronze, and by Schleicher² on the hot pressing of bronzes of various tin contents. At that time it was common practice in industry to cast bronze in small, comparatively thin strips for cold rolling to sheets, and to make all but the largest rods by cold rolling billets. Some companies achieved a measure of success in hot rolling larger rods, probably by machining the surface off the billets and by using powerful rolls. Even so, it was usual to restrict the tin content to a maximum of about 3%, alloys containing 1% or 2% being common.

More recently work by Lepp³, Pell-Walpole,⁴ Chadwick,⁵ and others has indicated the importance of porosity (of both the gaseous and fissure types), of tin sweat, and of impurities on the working charac-

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teristics of bronzes. These factors will be discussed in some detail later. Although improved techniques, especially in casting but also in fabrication, have enabled bronzes with tin contents up to 7 or 8% to be hot worked comparatively easily, and bronzes with tin contents up to about 16% to be made commercially, it still appears that bronzes are both intrinsically harder to work, and capable of being worked in a narrower temperature range, than many other copper-base alloys.

It is proposed in the present paper to examine some of the theoretical considerations which apply to the problem, then to discuss the more practical aspects of the effect of casting conditions on the material to be hot worked, and finally to describe briefly successful methods of hot rolling and extruding tin bronzes.

II.—THEORETICAL CONSIDERATIONS.

Examination of the copper-tin equilibrium diagram,⁶ shown in Fig. 1, suggests that there should be no great difficulty in hot rolling material containing up to about 15% tin at temperatures of the order of 700° C. Under these conditions the structure should be all α , or α with a little β , and both the α and β phases are reasonably tough and malleable at elevated temperatures. The brittle δ constituent, which causes some difficulty in cold working the higher-tin bronzes, is unstable at temperatures above 520° C. There seems to be little doubt, however, that the α phase becomes less ductile as the temperature is raised, though the reasons for this are not yet fully understood.

The use of some deoxidizing agent is necessary in the production of a sound bronze casting for subsequent working, in order to avoid inclusions of metallic oxides, especially tin oxide. The most commonly used deoxidizer is phosphorus. To effect satisfactory deoxidation, the residual phosphorus content of the bronze should not be less than 0.02%; the upper limit is fixed by the requirements of use and the method of fabrication. A high phosphorus content in a bronze increases the tensile strength and hardness, and also increases the rate of work-hardening, but will lead to trouble if the material is hot worked. Verö⁷ studied the diagram of the ternary system copper-tin-phosphorus, and published vertical and horizontal sections of the copper-rich corner. The sections parallel to the tin axis are shown in Fig. 2. It will be seen that with 10% tin and 0.5% phosphorus a liquid constituent is present at 637° C. Even with 5% tin, about 0.8% phosphorus is all that is needed to produce a liquid phase at about 660° C. Now these figures apply to material in equilibrium, and it is unlikely that commercial castings will be in equilibrium when they are reheated for rolling or

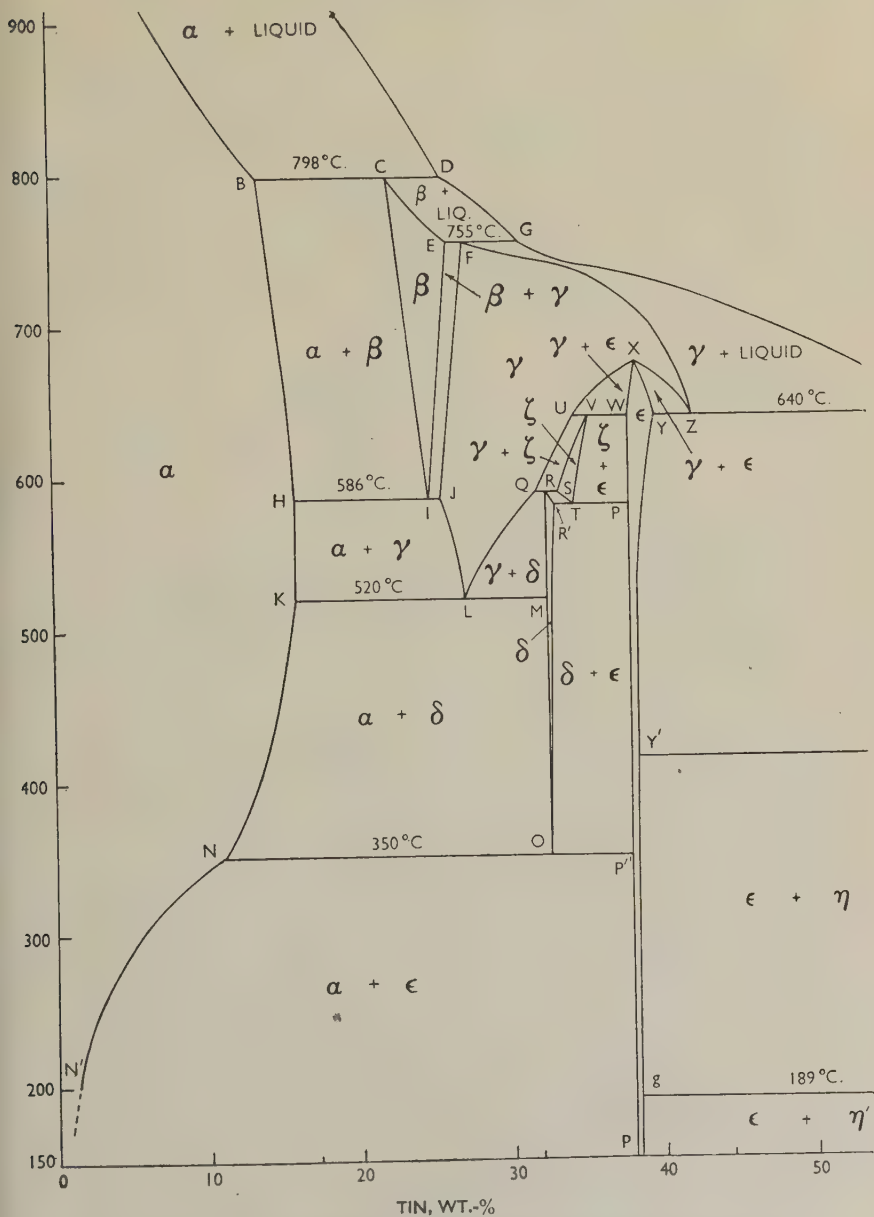


FIG. 1.—Copper End of Copper-Tin Constitutional Diagram (after Raynor⁶).

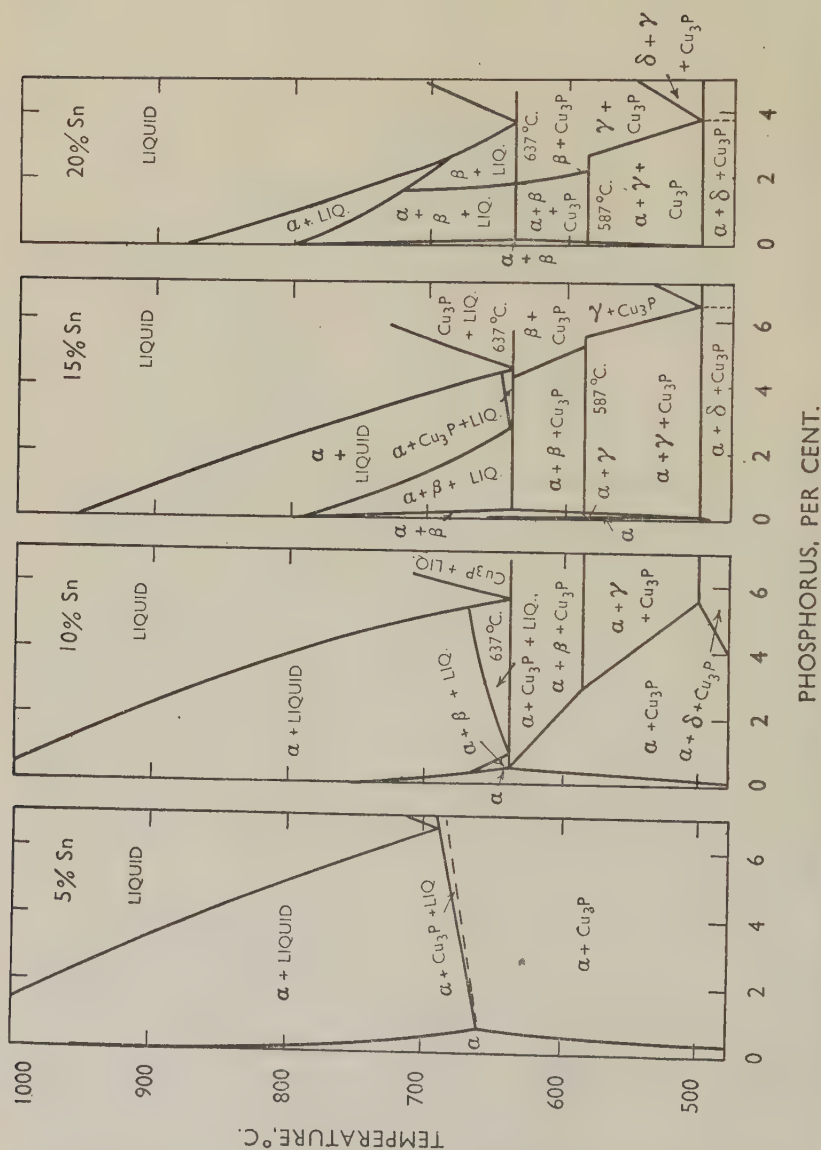


Fig. 2.—Vertical Sections through Constitutional Model of the Copper-Tin-Phosphorus System (after Verö 7).

extrusion, because of the slowness of diffusion. Thus the permissible phosphorus limit for material to be hot worked is generally taken to be much lower than the equilibrium diagrams indicate.

Although examination of these diagrams suggests that the hot working of bronzes should not be difficult, the restricted upper limit to the working temperature range, the possible formation of the metastable copper-phosphorus-tin complex, and the intrinsic weakness of the α solid solution at elevated temperature, make the phosphor bronzes one of the most difficult types of copper-base alloys to hot work successfully.

III.—CASTING.

The importance of the application of certain principles and of attention to detail in the casting of bronze for subsequent hot working cannot be over-emphasized.

The Effect of Impurities.

In the first place, very pure materials must be used to make up the charge. The copper used should be electrolytic, or high-grade fire-refined ingots containing at least 99.92% copper. Lead, bismuth, and antimony should be absent or present only as traces. One of the most marked improvements in the hot-working capacity of bronze resulted from the introduction of the Chempur brand of tin. In fact, it is true to say that at many works the advent of this pure tin enabled bronzes to be made for the first time which could be hot worked commercially.

The alloys first produced with this material mostly contained 5% or less of tin, it being assumed with some justification that higher-tin bronzes would be harder to hot work without cracking. There has been no published account of the effect of small amounts of impurities on the hot working of bronze, but examination of typical analyses for Chempur tin and five standard refined tins given in Table I suggests that lead and bismuth are the impurities most likely to be deleterious. It should be noted that it was not universal, or even general, practice to use refined tin for bronze making; common tin, containing about $\frac{1}{2}\%$ lead, together with other impurities, was often used. Analyses of two typical samples of this material are included in Table I.

It is generally accepted that if bismuth is present in phosphorus-deoxidized non-arsenical copper in amounts in excess of 0.003%, cracking is likely to occur when the copper is hot worked. Further, if hot working is to be carried out at temperatures between 400° and 700° C., the permissible limit for bismuth is 0.0015%. These limiting figures for bismuth are quoted in the relevant British Standard Specifications.

TABLE I.—*Analyses of Various Grades of Tin.*

Impurity	Chempur Tin	Standard Refined Tins					Commercial Tins	
		A	B	C	D	E	F	G
Copper, % . . .	0.0005	0.0014	0.012	0.0360	0.0016	0.0743	0.061	0.129
Lead, % . . .	0.0030	0.0371	0.038	0.0601	0.0110	0.0582	0.468	0.386
Bismuth, % . . .	0.0005	0.0048	0.003	0.0026	0.0019	0.1600	0.012	0.019
Antimony, % . . .	0.0055	0.0210	0.040	0.0233	0.0067	0.0200	0.136	0.190
Arsenic, % . . .	Nil	0.0113	0.060	0.0500	0.0020	0.0150	0.065	0.078
Iron, % . . .	0.0020	0.0170	0.002	0.0110	0.2055	0.0065	0.006	0.006
Zinc, % . . .	Nil	Nil	Trace	Nil	Nil	0.0004
Silver and Gold, % .	Nil	Nil	0.0003	0.0005	Nil	0.0024	0.008	0.012
Sulphur, % . . .	Nil	0.0015	0.0003	0.0060	0.0039	0.0034
Total Impurities, %	0.0115	0.0941	0.1456	0.1895	0.2326	0.3402
Tin, by difference, %	99.9885	99.9059	99.8544	99.8105	99.7674	99.6598	99.206	99.158

Examination of the analyses of the standard refined tins given in Table I shows that they contain bismuth in amounts between about 0.002 and 0.005%, except for one example which contains 0.16%. If one of these tins is added to pure copper containing virtually no bismuth to make an alloy containing 5% tin, the bismuth content of alloys made from standard tins *A* to *D* will be of the order of 0.00015%, while with tin *E* the bismuth content will be 0.008%. Now it is quite reasonable to suppose that an addition of tin does nothing towards removing the embrittling effect of over 0.003% bismuth in copper, so it is to be expected that a bronze made from tin *E*, containing 0.008% bismuth, would not hot work satisfactorily, but the bronzes made from tins *A* to *D* contain only 0.00015% (an amount $\frac{1}{20}$ th of that necessary to cause cracking in copper). It is unlikely that this small amount would be responsible for the failure of the bronze. Not all the tins used to try to make bronzes which would hot work were similar to tin *E*, so that some other cause of the general failure to hot work bronzes must be sought.

If a similar argument is followed through for lead, contents of the order of 0.0025% will be present in 95 : 5 bronze made from refined tins. It is generally agreed that the lead content of deoxidized copper which has to be hot rolled must not exceed 0.02%,⁸ and here again it is unlikely that additions of tin will remove the embrittling effect of lead. It would appear then that the lead contained in the refined tins cannot *per se* be the cause of cracking in hot-working bronzes made from these tins. Similarly, a 95 : 5 bronze made from one of these tins will contain about 0.0015% antimony, though it is unlikely that this by itself will cause brittleness.

Bronzes made from the common tins, however, will have lead contents of the order of 0.03%, bismuth of the order of 0.001%, and antimony of the order of 0.007%. Of these three, lead exceeds the

permissible allowance of 0.02% for deoxidized copper, and is probably the chief cause of the cracking.

It is well known that bronze castings are liable to suffer from a defect known as "tin sweat", the influence of which on the hot-working properties, and the methods for its prevention, will be discussed below. If entrapped or dissolved gases have the power of carrying high-tin material through interstices between the grains of the solidifying alloy, because of the low freezing temperature of this material, it seems likely that in a similar way, any eutectics, compounds, or impurities with a low melting temperature will be carried towards the surface of the casting. It is to be expected that metastable ternary or quaternary eutectics may be formed from the small quantities of lead, bismuth, and antimony present in refined tin in combination with the tin itself, and, of course, all these metals, except antimony, have a very limited solubility in copper and melt at comparatively low temperatures. These constituents will be forced towards the surface as the liquid mass solidifies, and some traces of them are likely to be trapped as intergranular impurities, which, having a low melting temperature, will cause hot shortness of the typical intercrystalline type associated with bronze.

This explanation of the increased difficulty in the hot working of bronzes made from refined tin as compared with bronzes made from Chempur or similar tin seems the most likely one. Confirmation is obtained from an examination of the amounts of the harmful impurities in Chempur and similar grades of tin, which are of the order of $\frac{1}{20}$ th to $\frac{1}{100}$ th of the amounts present in refined tins, and hence, are unlikely to be present in sufficient quantities in the bronzes made from these tins to have any significant influence on hot shortness. A logical deduction from this argument would be that a bronze melted and cast under such conditions that there was no evolution of gases on solidification, should be capable of subsequent hot working even if made from a refined tin such as *A* to *D* quoted in Table I, because the distribution of impurities due to normal segregation should not be so harmful as the distribution caused by inverse segregation. Some experiments designed to check this argument tend to confirm that this is so, but insufficient work has yet been done to be certain. It would seem, however, that material free from porosity of all types is much less sensitive to small amounts of many impurities, including aluminium, silicon, and manganese, than material containing the usual gas- and shrinkage-porosity.

The Effect of Tin Sweat.

Reference has been made to tin sweat, the influence of which on the hot-working properties of bronze is marked. The causes of and

remedies for tin sweat have been dealt with very fully by Lepp,³ Baker and Child,⁹ Pell-Walpole,⁴ and others,¹⁰ and it is not intended to discuss them at any length here. There is no doubt that degassing the melt by oxidation or some similar means, followed by casting at a slow controlled pouring rate, does produce a bronze sounder and more easily worked than one melted and poured in the ordinary way. Other considerations, however, enter when material is being produced commercially, and sometimes a casting sufficiently sound and malleable can be made without the application of any special technique. As an example, 95:5 bronze billets for extrusion can be made quite successfully by melting quickly in a coke-fired pit furnace, and pouring directly into a vertical mould, provided such factors as casting temperature and cleanliness of the melt in the pot are controlled carefully. Billets made in this way have no sign of the grey colour indicative of tin sweat, and if there is any segregation of tin or impurities towards the surface, it is removed in the extruding operation. Similarly, large cakes weighing up to 3 tons may be cast vertically from metal melted in coke-fired pit furnaces quite successfully, in alloys containing up to about 7% tin. Again, no indication of tin sweat is visible provided care is taken. Castings of this nature would normally be machined before rolling whatever copper-base alloy they were made from, so again any surface layer produced by segregation is removed. It is interesting to note that if a casting of this type is rolled without machining, as sometimes occurs when material is required for internal use as pickling trays, no undue cracking troubles are encountered and the hot-rolled material looks quite good and sound. Scraping or machining, however, reveals traces of grey tin-rich constituent just under the surface, which is an indication that exudation of the tin-rich material has occurred to a limited degree during solidification. For billets for hot rolling into rods, especially where no machining is done on the casting before rolling, degassing or slow pouring does offer marked advantages. Cracking troubles are less, and a product with a better surface results.

IV.—HOT-WORKING OPERATIONS.

Forging.

Chadwick⁵ has investigated the hot-forging characteristics of an extensive series of binary tin bronzes and ternary phosphorus bronzes on a laboratory scale. He worked with tin contents up to 30% and phosphorus contents up to 0.5%, and hot forged at various temperatures specimens made from sound degassed material in a hydraulic press at a rate of 8 ft./min. from 0.5 in. dia. by 0.5 in. high to a height of 0.2 in.

The amount of cracking was recorded on an arbitrary scale on which 0 represented complete freedom from cracks, whilst 6 represented a sample in which cracks reached the centre of the forging and 7 represented a sample completely shattered to powder. Figs. 3, 4, and 5, taken from Chadwick's paper, illustrate the results. Bronzes with no phosphorus or other deoxidizer are not made for hot working com-

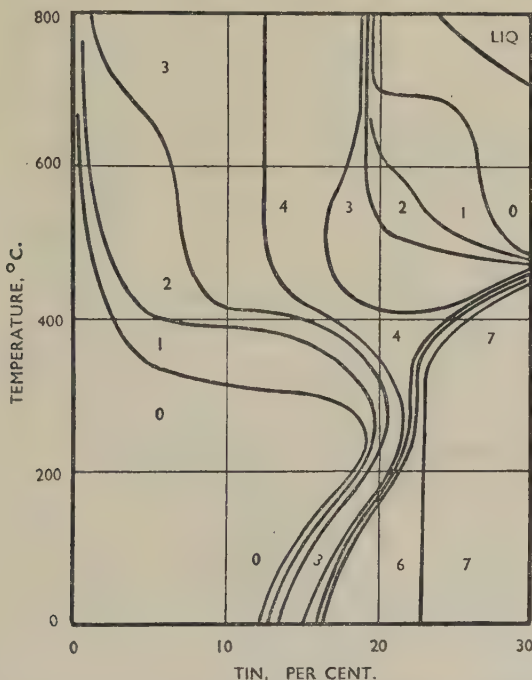


FIG. 3—Hot-Forging Tests on Cast Cylinders of Phosphorus-Free Bronzes. (after Chadwick⁵).

mercially, so the diagrams illustrating the forging properties of material containing 0.1% and 0.5% phosphorus are the more important. Examination of Fig. 4 shows that reasonable forging characteristics were obtained with bronzes containing up to about 6% tin at all temperatures up to 800° C., whereas the higher-tin bronzes up to about 13% tin tended to crack at temperatures above about 350°–400° C. There was a very tough region, however, for bronzes containing 20–30% tin within a comparatively closely defined range of temperatures around 650° C.; material of this composition is unworkable at lower temperatures. Increase of the phosphorus content to 0.5% restricted the temperature

and tin content of both these tough areas, bronzes with over about 3% tin cracking at all temperatures above about 400° C.

It is important to bear two considerations in mind when examining Figs. 3-5; one is that forging unsupported cylinders is probably a more severe test on the material than that imposed in commercial rolling or extrusion operations, a fact that is borne out by Chadwick's own success

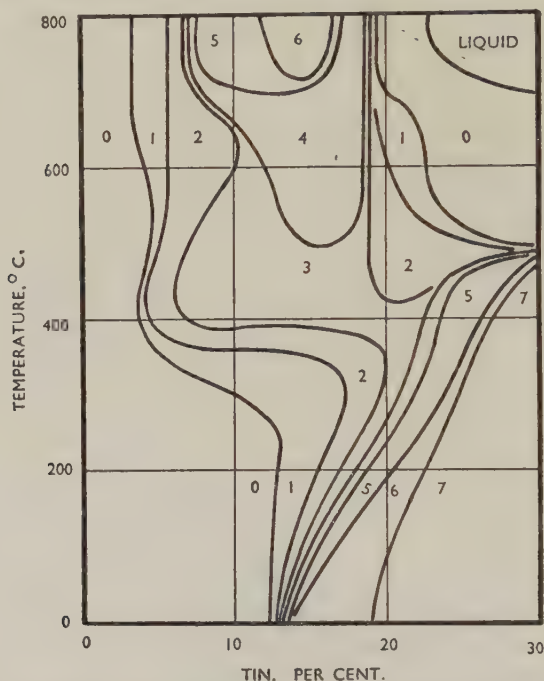


FIG. 4.—Hot-Forging Tests on Cast Cylinders of Bronzes Containing 0.1% Phosphorus (after Chadwick⁵).

in hot rolling all his alloys at selected temperatures excepting those in the range from about 17 to 19% tin. The other is that to be a successful commercial process hot working must be carried out at a sufficiently high temperature to obtain all or most of the advantages of hot work as opposed to cold work; that is, that the material must be plastic, have a low resistance to deformation, and be well above the recrystallization temperature. These latter conditions would not be satisfied by hot working, say, a bronze containing 10% tin and 0.1% phosphorus at 350° C. It is probably this consideration that led to Stokeld's¹¹ stating that only bronzes containing up to 2% tin and 0.1% phosphorus could be hot forged commercially.

Hot Rolling.

The hot rolling of bronzes with a low tin content does not present great difficulties provided that the cast ingot is satisfactory. Collier,¹² discussing Chadwick's work, stated that it was well known that bronze containing 1% tin and only traces of the deoxidizing element would hot

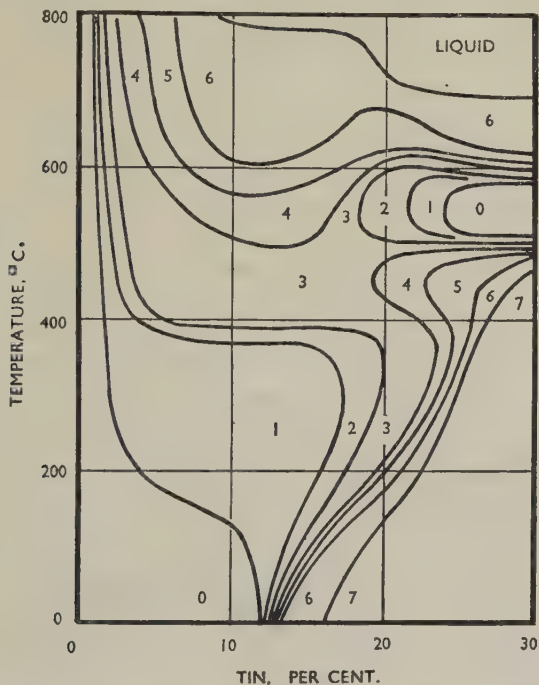


FIG. 5.—Hot-Forging Tests on Cast Cylinders of Bronzes Containing 0.5% Phosphorus (after Chadwick⁵).

roll over a wide temperature range from 850° C. downwards. He stated further that 5% tin bronze with 0.05% phosphorus would hot roll satisfactorily at 600°–650° C., either from 7-in.-dia. billets or from 3 or 4 in. thick slabs. Brazener,¹³ in the same discussion, stated that he had had some success with hot rolling 97 : 3 copper-tin alloy within a narrow temperature range of approximately 550°–600° C.

In the present author's experience this upper limit of temperature is very important : not only should the temperature at which hot rolling is begun be carefully controlled, but the casting should not be raised to a higher temperature in the preheating muffle. If this has been done to any marked extent, great difficulty will be experienced even though the

material is cooled before hot rolling, as it will tend to crack up with an intercrystalline fracture. In this respect bronze differs from both copper and the usual hot-working brasses. The lower temperature limit is obviously imposed by the inherent resistance of the material to deformation, in conjunction with such factors as the strength of the available rolls and the economics of the operation. It is also desirable to soak bronze at the hot-working temperature for sufficient time before beginning to hot work both to ensure uniform heating through the casting and to take into solution any tin or phosphorus compounds that may exist in the cast material in an unstable or metastable condition.

Vertical bronze castings up to 3 tons in weight, and containing tin up to about 7% and phosphorus up to about 0.1%, can be hot rolled without much difficulty provided that the plant is sufficiently powerful. The reductions which can be given to this material are of the order of 25% of those for a similar yellow-metal casting. Rolling can be continued until the metal is black without causing cracking. After the initial breaking-down it is possible to reheat the material to a higher temperature, about 650°–700° C., for the subsequent hot-rolling operations.

It was mentioned earlier in discussing forging that bronze when deformed hot tends to crack at any unsupported places. This effect is not very serious in the hot rolling of plates, because at the worst it leads only to slight edge cracking. In the hot rolling of rods, however, it may lead to cracking on the unsupported part of the billet between the grooved rolls, and this cracked material will subsequently be rolled into the rod. In addition, the rolls used for rod rolling are normally less powerful than those used for plate rolling, so greater attention must be paid to the production of the billets and to their preheating.

Extrusion.

The limitations already discussed apply to the extrusion as well as to other forms of hot working of bronzes. The bronzes require more pressure to extrude, and must be extruded within a narrower temperature range, than copper or most other copper-base alloys; but, even so, extrusion is a valuable process for the hot fabricating of rods and tubes in smaller sizes. Bronzes containing about 5% tin and under 0.1% phosphorus can be extruded at about 800°–850° C. with success provided that the extrusion speed is controlled carefully; too high a speed will produce cracking in the extruded product, while too low a speed will allow excessive heat loss with consequent fall in temperature, which in turn will stop the operation. Attempts to extrude at too high a temperature will cause serious peripheral “fire cracking”, which in the

limit may lead to complete disintegration of the product. It is not normally the capacity of the bronze to withstand deformation at lower temperatures that dictates the lower limiting temperature of extrusion, but rather the power available in the presses; in fact, one of the major problems to be faced in producing bronze extrusions is the narrow working range between the temperature at which the bronze cracks and the temperature at which it will not extrude at all. Obviously, the size of press, the size of the product, the number and shape of the holes in the die, and the speed of extrusion all influence the extent of this temperature range. The difficulty is intensified when bronzes with higher tin contents are extruded, so that while material with, say, 14% tin has excellent physical properties, it is not always a commercial proposition to produce it. Great care is needed with high-tin bronzes, and the results obtained are not always reproducible, but bronzes containing up to about 8% tin with about 0.25% phosphorus can now be extruded satisfactorily.

In the extrusion of a 95 : 5 bronze, the time cycle of the pressure applied to the billet in the press differs from that for a brass, or indeed from that for most other copper-base alloys. This is illustrated by a comparison of the pressures applied to the ram at different times during the extrusion of, say, 45 × 55 mm. tube from 6-in.-dia. billets in 60 : 40 brass and in 95 : 5 bronze. With the brass, extrusion starts when a reasonably high pressure is applied, and continues with the application of a steadily increasing pressure until the internal friction in the metal rises sharply, thus producing a marked increase in pressure and indicating the completion of the process. With a bronze, however, a very much higher pressure is needed to start the extrusion, after which the pressure is reduced considerably until more than half the billet has been extruded, when it increases steadily to the end of the process as before. The true reason for the necessity of the high initial pressure is not obvious, but the observation does confirm that bronze retains the superior resistance to deformation in the hot state which it shows in the cold.

V.—CONCLUSION.

Although it is quite possible to hot work phosphorized tin bronzes containing up to about 15% tin on a commercial scale, the necessity for very careful control of casting and fabricating conditions, together with the possible formation of a metastable copper-phosphorus-tin complex and the intrinsic weakness of the α solid solution at elevated temperatures, make these materials some of the most difficult of the copper-base alloys to handle.

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THE HOT WORKING OF LEAD AND LEAD-RICH ALLOYS.*

1231

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SYNOPSIS.

The sheathing of cable by both lead presses and extrusion machines is discussed, and a description given of the manner in which certain extrusion faults arise. The production of lead pipe, lead sheet, and collapsible lead tubes is reviewed, and the extent to which the hot working conditions are controlled in all sections of the lead-using industry is considered in the light of the service requirements of the individual products.

I.—INTRODUCTION.

WITH most metals and alloys there can be associated a certain temperature range within which, by a process of continuous recrystallization, they behave as plastic masses offering little or no increase in resistance to deformation as deformation proceeds; it is this ability of most metals and alloys to undergo extensive deformation unaccompanied by work-hardening that forms the basis of all hot-working operations. For many alloys this hot-working range of temperature is comparatively narrow, and it is in general bounded above and below by such factors as the onset of hot shortness and work-hardening. In the case of lead and its commoner alloys, however, it is difficult to make any ready differentiation between hot- and cold-working operations, for even at room temperature, a temperature normally associated with cold working, continuous recrystallization may occur simultaneously with deformation, and the process becomes, metallurgically speaking, a hot-working one; thus it is a fact that lead may be worked with extreme ease at all temperatures from just below the melting point to room temperature.

Generally speaking, most other non-ferrous industries are faced with considerable limitations when hot working, and have consequently been forced to a much more detailed study and application of the metallurgical fundamentals of the process than has been necessary in the lead industry. Lacking this impetus, it is rather the exception to find control exercised over the working processes to anything like the degree

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necessary in other branches, for the latitude permissible in all lead-forming operations is extremely large.

The manufacturers of wrought lead products can be divided into three main classes : one section concerned with the sheathing of electric cables, another with the manufacture of lead sheet and pipe, and the third with the impact extrusion of collapsible tubes. Relative lead consumption falls in the same order, and in view of the generally different requirements of the finished products it has been thought desirable to maintain the same division in the present paper. Battery grids, which constitute a large proportion of the industrial outlet for lead, are castings.

For the convenience of those unfamiliar with lead-working practice, there is included under each heading a brief description of the plant and working process employed ; this is followed by accounts of the defects which may occur in the products and which arise from the method used, and of the ways in which some variables in the working processes may be controlled to attain desired properties in the finished material.

II.—CABLE SHEATHING.

1. *Plant and Process.*

The outstanding properties of lead from the cable manufacturer's point of view are its high corrosion-resistance, its imperviousness to moisture, and the extreme plasticity which permits its direct extrusion around a cable core at temperatures which do not harm the insulation. The forming operation is thus one of extruding a continuous tube of lead or lead alloy around a central core, and the problems immediately associated with this process are two, namely the production of a long sheath free from discontinuities and the maintenance of a specific wall thickness of lead sheath.

Broadly speaking, cable sheathing is carried out with one of two types of equipment, either with the conventional direct-extrusion cable press, or by means of the continuous-extrusion machine, the former being the more widely used. As some attention must be given to the mechanics of the extrusion processes involved, in order that the origin of such faults as do arise in manufacture may be appreciated, a brief description of both types of equipment and the operational techniques employed is given below. For a very full account of the extrusion process and the different types of press in use in the industry, reference should be made to Pearson's book.¹

In the case of the more common cable press a container of some 5-15 cwt. capacity is mounted vertically above a die-box which con-

stitutes the forming chamber and which houses a laterally disposed point-holder and die-ring. The point-holder is in the form of a hollow mandrel through which the cable is fed, and carries at its extremity a detachable point which, in conjunction with the die-ring, forms the extrusion orifice through which the charge is pressed. Thus the axis of the press ram is vertical and the ultimate direction of metal flow horizontal. Lead is charged into the container through an open chute from the melting-kettle and the dross skimmed off the surface of the molten billet before bringing it under slight pressure from the extrusion ram, which prevents the formation of a contraction pipe and minimizes further oxidation at the billet face. After solidification, the extrusion pressure is applied and the lead forced from the container into the forming chamber surrounding the point-holder. The sheath issuing from the orifice grips the cable which is thus drawn through the hollow point-holder. When the greater portion of the charge has been extruded, the container is retracted, a fresh charge poured on top of the residual slug, and the procedure repeated. Thus by intermittent operation, a continuous length of sheathing may be extruded.

Two extrusion machines, both developed at about the same time, were in operation in the early 1930's producing lead sheathing by a process designed to eliminate the difficulties associated with the intermittent extrusion operation briefly described above. The two machines, the Henley and the Pirelli continuous-extrusion machines, operate on the same principle and differ only in features of design. The Pirelli machine is the more widely used, and in this an impeller in the form of a cylindrical sleeve, carrying helical ridges on both inner and outer surfaces, rotates in an annular space between a stationary point-holder and an outer barrel. Longitudinal slots machined along the bore of this barrel and on the outer surface of the point-holder, serve to key, against rotation, the metal which is admitted to the two annular spaces running between the impeller and the stationary members. The lead is admitted through a closed pipe to one end of the machine and is progressively solidified in the screw channels by water coolers running the length of the barrel and point-holder, and it is finally delivered in two streams to the forming chamber housing the point and die-ring. The sheath emerging from the extrusion orifice grips the cable and draws it through the machine in the same manner as with the conventional press.

2. Origin and Remedy of Defects Inherent in the Process.

The faults which at one time were most prevalent in cable sheathing and to which a large proportion of ultimate failures could be ascribed,

are directly attributable to the method of fabrication employed in the cable press. They arise as the result of turning the metal flow through 90° from the press centre line and are consequent upon the repeated charging of new billets on top of residual slugs. The conventional vertical press uses either a single- or twin-entry die-box, both of which give rise to characteristic faults in the extruded product. In the simplest arrangement, the single-entry box, lead flows downwards from the container and divides over the laterally disposed point-holder into two streams which meet and weld below the point-holder and subsequently pass along it in a horizontal direction towards the extrusion orifice between the point and the die-ring. In the twin-entry die-box, however, two streams are led from the container to entry ports disposed on opposite sides of the forming chamber and the lead passes around the point-holder forming welds both underneath and above it. Thus, continuous longitudinal welds are produced in the sheathing which issues from the die.

Although satisfactory pressure-welding is not necessarily dependent upon grain growth across the weld interface, really sound welds are produced in cable sheathing only when recrystallization and grain growth take place across the boundary face between the confluent streams of metal in such a way that the final distribution of oxides present at this interface is primarily transcrystalline. Dross present in the extrusion chamber tends to segregate along the flow lines of the metal, and a large percentage finds its way to the outside of the lead streams flowing into the forming chamber, and thus interferes with welding. First attention, therefore, has been in the direction of eliminating, as far as is practically possible, all dross and oxides from the extrusion charge. Apart from that which may be carried over from the melting-kettle and subsequently be entrapped in the body of the billet, inclusions may originate in either of two places, namely at the top end of the cast billet in contact with the extrusion ram, or at the junction between successive charges.

The type of flow which occurs in the cable press is usually described as direct-extrusion flow, and gives rise to a fault which, in its severest form, is known as the "extrusion defect". It is not difficult to picture how this fault arises as a result of frictional effects and because of the temperature and, therefore, plasticity gradient which exists across a diameter of the cooling billet. Flow takes place much more readily from the softer core of the billet, which is also relatively freer from frictional forces, and at a certain stage of the extrusion the flow region will extend to the far end of the billet in contact with the ram, and material from this face will be drawn into the extrusion flow. It is thus

of paramount importance to ensure that a minimum of dross and oxide is allowed to remain at the top of the billet on solidification, and it is for this reason that the surface of the molten billet is well skimmed before setting it under pressure from the ram.

It is the junction between successive charges, however, which gives rise to the severest contamination. On completion of the extrusion stroke, the ram is retracted relative to the container, and leaves a residual slug of metal in the base of the container on to which the subsequent billet is cast. Much of the dross left to freeze at the top of the previous billet will remain on the face of this slug, and unless special precautions are taken on recharging, there will remain after solidification a transverse layer of dross and oxide between the new billet and the old slug. On passing through the forming chamber, this stratum of oxide gives rise to a fault known as lamination. Apart from the presence of such inclusions at confluent surfaces preventing welding, the initial stratum of oxide is drawn out into a long tapering tongue which may extend for a hundred feet or more of product length, and which effectively laminates the metal forming the sheath. In general, this lamination does not severely impair the mechanical strength of the sheath, providing it is absent from weld junctions, and if, as is usual, it extends for some great length, it in no way lessens the effectiveness of the sheath as a moisture barrier, particularly in view of the fact that rarely does the lamination actually break the surface of the sheath. There is a loss in ductility, however, and for such applications as oil-pressure-filled cables this loss may result in immediate failure on pressure loading, when sufficient ductility is required to permit the lead sheath to creep radially and transmit the loading to the surrounding armour.

Mention should be made of two methods of working with the cable press which effectively reduce the prevalence of laminations and weak welds. In the one case, molten lead is fed from the melting-kettle through a closed pipe, thus reducing oxidation during pouring, and directed on to the face of the old slug by means of a stand-pipe. The flow of hot metal flushes away the dross and oxide from the face of the slug and exposes a clean surface to the following charge, the inclusions rising to and being skimmed from the top of the molten billet. In the other method an attempt is made to cast and work the lead *in vacuo*. On the top of the container and surrounding the lead ram, is placed a large gas-heated vessel which is kept charged with molten lead from the melting-kettle. Between the ram and the vessel there is a molten-lead seal which forms a barrier between the atmosphere and the container bore. The capacity of the vessel is just greater than that of the

container, and on completion of the extrusion stroke the container is gradually retracted and towards the lower limit of its stroke a series of inlet ports which connect with the bottom of the vessel are uncovered by the ram and admit a fresh charge of lead to the container. Oxidation is thereby largely avoided. Sections of products extruded in this manner show very few inclusions, and those present at the weld positions occur within the crystals rather than on the plane of the original weld interface.

The continuous-extrusion machines were designed to overcome these difficulties with the semi-continuous cable sheathing press, and they do in fact eliminate troubles attributable to oxide inclusions. However, in spite of the straight-through flow of metal which takes place in the extrusion machine, rigid support has to be afforded to the overhung end of the point-holder to ensure that the required tolerances on wall thickness are met. This support is provided by a spider block consisting of three or four arms radially disposed between the point-holder and machine frame, the arms dividing the flow of metal from the screw into three or four streams which are subsequently united and welded in the forming chamber. The number of longitudinal welds produced in the cable sheath is therefore increased from the one or two produced in the cable press to, possibly, three or four, but in view of the fact that at no stage in its passage from the melting-kettle and through the machine is the lead exposed to the atmosphere, little oxidation of the lead can occur, and generally remarkably clean, sound welds are produced. Lamination is, of course, entirely eliminated in this continuous method of extrusion. Soundness of the welds is in part attributable to the higher operating temperatures employed in the extrusion machine, which may be of the order of 250° – 300° C. at the die, compared with the cable press working at 200° – 250° C. There are attendant difficulties of operation, however, for an extremely careful balance must be maintained between water cooling, subsidiary heating, and screw force, and this demands considerable skill from the operator.

A characteristic of the continuous product, which may hardly be called a defect as it would appear to have no deleterious effect upon the mechanical properties, is the appearance of what may be termed "whirl-lines", in the structure seen in cross-sections. It would seem that solidification of many of the cable alloys under extreme mechanical disturbance in the screw channels is accompanied by a high degree of segregation, notably with the antimony and antimony-tin type of alloys. Thus, the heavily segregated solid issuing from the screw channels, passes into the forming chamber accompanied by a heavy shearing of one section of flow over the other and moves on towards the

ports in the spider-block in the form of thin transverse layers of segregated material from one screw channel after the other. On passing through these ports, the layers are drawn out longitudinally, so that on etching a section of the product concentric rings appear between the positions of the spider arms, as illustrated in Fig. 1 (Plate LXXV). The rings are merely an etching effect brought about by the variable composition resulting from segregation, and may be dispersed on prolonged ageing at elevated temperature.

Considerable difficulty is experienced with both cable presses and machines in maintaining a sheath of constant wall thickness. Owing both to mechanical and thermal straining of the point-holder, eccentric sheath may readily develop with varying conditions of pressure and temperature, and carefully controlled working conditions are called for in avoiding this trouble. In the vertical, direct-extrusion press, employing a single-entry die-box, considerable downward pressure is exerted on the point-holder; this, coupled with the fact that the lead feeding the underside of the holder has a far more tortuous passage to pass along, with greater frictional forces at play due to the generally colder press components, often leads to a progressive thinning of the underside wall-thickness. Twin-entry die-boxes in large part remove these difficulties by providing equally balanced flow at opposite sides of any given diameter. To facilitate uniform flow, however, it is usually the practice to provide local heating in the neighbourhood of the die-box.

The occasional advent of faults directly attributable to the extrusion process are now less a cause of concern to the industry than the inherent weakness of the material itself, and the extent to which the working operation may be varied to produce more desirable properties is considered in the next Section.

3. *The Effect of Some Hot-Working Variables on the Properties of Cable Sheaths.*

The service conditions of cables vary enormously from one type to another and considerable research effort is being devoted to an attempt to analyse these individual conditions and, at the same time, develop improved alloys with properties better able to withstand the particular stressing involved. To illustrate these varying requirements consider, say, the service conditions of an oil-pressure-filled cable and an overhead telephone cable. Pressure-filled cables, which operate with internal oil pressures of up to 60 lb./in.², require a lead sheathing which is sufficiently ductile to creep radially and transmit the oil-pressure loading to the armoured sheath surrounding the lead. Emphasis in this case is thus initially upon extreme ductility. Subsequent service,

in this and other types of power cable, requires resistance to the slow-cycle fatigue induced thermally by periodic load fluctuations. This latter condition falls somewhere between the normally accepted fatigue-type stressing and creep conditions, and as improvement of one property does not necessarily imply improvement of the other, difficulty is sometimes experienced in specifying the correct alloy to withstand this type of service. In the case of overhead cables, vibratory strains induce a stress condition which is predominantly of a fatiguing nature, and here emphasis falls upon high fatigue-resistance.

Fatigue properties of lead may be improved greatly by alloying and, according to Beckinsale and Waterhouse,² would appear to be sensibly independent of grain-size. The creep properties of lead and its alloys, however, have been shown to be remarkably dependent upon grain-size,³ a characteristic shared by other materials at temperatures high in relation to their melting point, and it may be said that, all other factors being equal, over a wide range of sizes the smaller the grain-size of the material under stress the poorer its creep-resistance, but the greater its ductility as indicated by its extension to failure. In general, therefore, a fine, even grain-size is desirable for lead sheathing to ensure adequate ductility and resistance to fatigue.

The alloying of lead for improved properties is usually associated with a certain degree of grain refinement and, in general, a fine grain-size is automatically obtained. With certain alloys, notably Alloy *E* (0.4% tin, 0.2% antimony), considerable grain growth is liable to occur subsequent to extrusion, with consequent loss in ductility, and to prevent this water quenching of the product immediately after extrusion is often employed.

The extrusion temperature employed in most cable presses is of the order of 200°–250° C., being maintained as high as possible to facilitate welding in the forming chamber, and at such temperatures little difficulty is experienced in extruding the alloys in common use through reduction ratios of 100 : 1 or more. Control of extrusion temperature is more important for some alloys than others. In particular, alloys of the 0.85%-antimony type contain a eutectic phase after solidification in a cable press or an extrusion machine; this phase liquefies if the nominal extrusion temperature or rate of extrusion is raised too high and the resulting hot shortness causes cracking in the extruded material. The melting point of the binary lead-antimony eutectic is 256° C., and relatively low operating temperatures are usually necessary in avoiding such hot shortness, particularly in the extrusion machine, where it would seem that segregation of antimony aggravates the difficulty.

The inter-relation of the variables of pressure, rate, and temperature of extrusion have been empirically established for lead by several workers using the simpler inverted-type flow, in which frictional effects between container and billet are substantially eliminated. Even with the simplest form of direct extrusion as employed in the majority of non-ferrous industries, however, the extrusion loads are in large part determined by such factors as the billet length and the presence of oxide scale, which may modify the flow considerably. It thus becomes impossible to deal with a specific extrusion pressure in the case of cable-sheath extrusion, as an even greater resistance is offered to metal flow and this naturally varies from press to press. Mention is made in a later Section of the correlations obtaining for the inverted extrusion of some lead alloys on an experimental press, and cable-type alloys are included for comparison.

III.—LEAD PIPE MANUFACTURE.

1. *Plant and Process.*

With relatively few exceptions, lead-pipe presses are of the vertical type and operate on the inverted principle of extrusion. In this method of working, the lead container of some 4 cwt. capacity is seated immediately upon the water ram, which is usually situated below floor level, and the billet is raised in the container against a hollow, stationary ram. The lower end of the container bore is closed by a 3-4-in.-thick block which serves as a seating for the core over which the lead is extruded. Billets are cast-in in the same way as for cable presses and generally allowed to solidify under slight pressure from the ram. As the container is raised against the die-plate held in the face of the ram, the billet is extruded from the container and the pipe passes up through the hollow ram and out of the press head. Extrusion is stopped when some 5% of the billet still remains in the container, in view of the greatly increased pressures required in producing what eventually becomes a predominantly radial flow. Removal of this slug from around the core and off the seating block is a lengthy operation and one which is only resorted to when a core or metal change is necessary; it is therefore allowed to remain in the base of the container indefinitely, and the new billets are repeatedly cast on top of it, producing effects which are described later. Of the alternative designs of press, there is only one which completely eliminates the faults associated with this method of working, and in this provision is made for ejection of the slug at the end of each extrusion.

2. Origin of Extrusion Faults in Lead Pipe.

The flow associated with inverted extrusion is confined throughout the whole extrusion to a region immediately in front of the advancing ram which is probably little more than the billet radius in extent. Several advantages accrue from this method of working, in particular the metal undergoes a much more uniform deformation than in the direct type of flow, both across any given section of the product and throughout the major part of its length. Although the extrusion defect is eliminated in this type of flow, it can be seen that, when towards the end of an extrusion the flow region in front of the ram extends to the base of the container, material from this face will begin to flow into the body of the remaining portion of the billet and will eventually be extruded. It is clear that on charging-in a new billet on top of the slug remaining from a previous extrusion, a layer of oxide and inclusions will remain to separate the two, and that towards the end of the subsequent extrusion this stratum of oxide will come within the region of flow before it becomes mechanically desirable to stop extrusion, in other words, before 95% of the billet length has been extruded. The oxide inclusions in the extruded product will appear initially as a ring of oxide near the inner wall of the pipe, but as extrusion is continued, the oxide ring appears nearer and nearer to the outer face of the pipe. Continual operation in this fashion will eventually lead to a heavily laminated slug remaining at the bottom of the container, and towards the end of each extrusion several of these strata of oxide may be drawn into the product. The polished, longitudinal half section of such a slug is shown in Fig. 2 (Plate LXXV).

The same trouble is encountered in direct-extrusion presses where these are used. The usual arrangement in such presses is for the die to be located in the base of the container with either a bridge core secured to the die-block or a short core carried on the end of a stout mandrel passing through the lead ram. At the completion of extrusion the slug remains at the bottom of the container surrounding the core and die and a new billet is cast on top of this. The slug is then partially extruded at the beginning of the following extrusion. The rejection of the first portion of the extruded charge corresponding to the weight of slug remaining at the end of extrusion largely avoids lamination in the finished product. In point of fact, however, the oxide stratum is drawn out to a far greater extent than this and may generally be seen as a dirty annulus of metal on the outside of much of the following extrusion.

Bridge cores are not widely used in the production of lead pipe in view of the possible seat of defects in the resultant longitudinal welds,



FIG. 1.—Segregation in Alloy *E* Pipe Extruded by Pirelli Continuous Machine.



FIG. 2.—Polished Longitudinal Half-Section of Laminated Slug.



FIG. 3.—Etched Cross-Section of Lead Pipe Showing Zoned Structure.

[To face p. 550.]

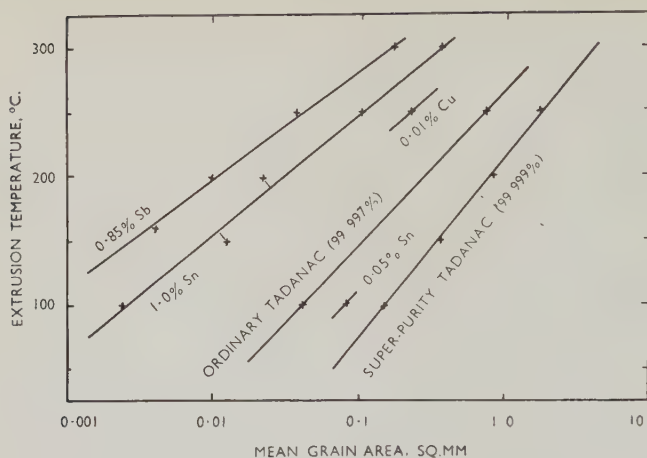


FIG. 4.—Relationship between As-Extruded Grain-Size and Extrusion Temperature for Constant Rate of Extrusion. Reduction ratio 21:1, rate of extrusion 10.5 in./min.

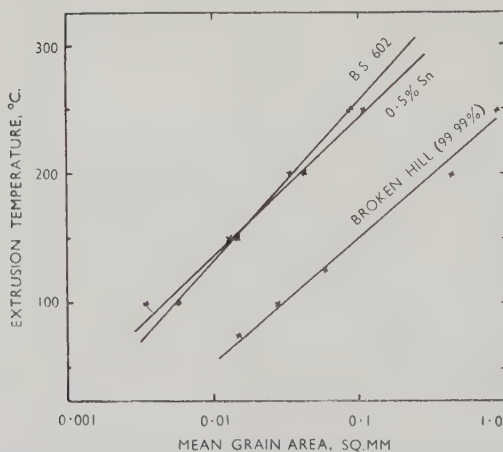


FIG. 5.—Relationship between As-Extruded Grain-Size and Extrusion Temperature for Constant Rate of Extrusion. Reduction ratio 21:1, rate of extrusion 5.25 in./min.

but with clean working and high operating temperatures those products extruded through bridge-core dies would appear to be as mechanically strong as those drawn over long cores.

3. *The Effect of Extrusion Variables on the Properties of Lead and Lead Alloy Pipe.*

High creep-resistance and good fatigue properties are required in all lead pipes required to withstand internal pressure. As was mentioned earlier, in any one material the coarser the grain-size the higher the resistance to prolonged stress, although the extension to failure under creep conditions is less for coarse- than for fine-grained materials. Consequently great importance is attached to obtaining such grain-size as will give the properties required to meet service conditions.

Mention has also been made of the grain refinement which is generally associated with the alloying additions commonly made to lead. Nevertheless, the alloys are usually much more resistant to creep than would be lead of the same grain-size, but the same variation in creep-resistance with grain-size is obtained. With some alloys it is extremely difficult to produce a sufficiently coarse grain to give the creep-resistance at low stresses equal to that given by pure lead with a grain-size of the order of 0.2 mm.², such as is readily obtained in accordance with B.S. 602.

The general effect of additions and extrusion temperature upon the as-extruded grain-size of lead and several of its alloys, is well illustrated by the results of some of the Association's current work given in Figs. 4 and 5 (Plate LXXVI). In these Figures the mean grain area of a $\frac{7}{16}$ -in.-dia. rod, extruded from a 2 in.-dia. billet, is plotted against the extrusion temperature for lead and lead alloys of various compositions. The trend is obvious, namely that for a given reduction ratio and rate of extrusion the as-extruded grain-size will be smaller, the lower the extrusion temperature and the greater the amount of any specific addition present. No useful purpose is served in studying these figures in greater detail in view of the small reduction ratio and extrusion speed employed, namely 21 : 1 and 10.5-5.25 in. of product/min., compared with the commercial practice for, say, a $\frac{1}{2}$ in. \times 7 lb./yd. pipe, where the reduction ratio may be 150 : 1 or more and the rate of extrusion between 30 and 60 ft./min. It is significant, however, that under the conditions of extrusion employed in these experiments, a 10 : 1 variation in grain-size could be obtained at any given extrusion temperature within the composition variation from a typical B.S. 602 alloy to a pure lead. British Standard Specification No. 602 requires that the composition of lead pipes to withstand internal pressure shall be not less than 99.80% metallic

lead and the material referred to as B.S. 602 in Fig. 5 in fact only contained 0.054% impurities. Thus, it is possible that wider variations in grain-size under the same extrusion conditions could be obtained within the limits of commercial production to this specification.

It is possible for the manufacturer to control the extruded grain-size to some extent by variation of the extrusion temperature or rate, but the effect of such variations as are economically or mechanically possible is far outweighed by the composition variation which is permitted, and it would seem that any attempt at a more rigorous control of grain-size than is at present demanded, must be accompanied by a more specific composition clause.

The conventional press lay-out necessitates leading the product over a pulley on issuing from the press-head and passing it down to floor level where it may conveniently be coiled on drums. The strain imposed on the hot pipe as a result of bending it over the pulley and then coiling is liable to result in recrystallization and grain growth with the consequent development of a characteristically zoned structure, see Fig. 3 (Plate LXXV). Failures of lead pipes are usually associated with such zoned structures. The zoned structure may be prevented from developing immediately if the product is water quenched as soon as possible after extrusion and before critical straining takes place. This, in fact, is the practice in the lead-pipe industry, where the product is led from the press head over as large a radius as possible and quenched before coiling. Although water quenching may in many cases inhibit immediate recrystallization, it is possible that subsequent ageing under service conditions will cause the ultimate development of this zoned structure.

A simple approximation to the load required for inverted-type extrusion at a constant rate and temperature is given by the expression :

$$p = ak \log_e (r)$$

where p is the extrusion load on the ram, a is the cross-sectional area of the billet, r the reduction ratio, and k may be termed the specific extrusion pressure of the particular metal at the temperature and rate of extrusion considered. The dependence of k upon extrusion temperature is illustrated in Fig. 6, where, for specific rates of extrusion, values of k are plotted against temperature. It may be seen that within the normal range of extrusion temperatures used in the lead-pipe industry, 150°–250° C., there is little difference between the extrusion loads required for any alloy which may fall within the B.S. 602 specification, possibly a figure of the order of 10% at the lower temperatures. Even the relatively hard 0.85% antimony alloy requires little more than twice

the extrusion pressure of pure lead. In general, the manufacturer of lead pipe is able to extrude an infinite variety of products in the commoner alloys by suitably adjusting temperatures and rates of extrusion and by occasional resort to alternative billet sizes.

IV.—THE ROLLING OF LEAD SHEET.

By far the greatest portion of the lead sheet output in this country is of refined lead of at least 99.5% purity with the total being made up

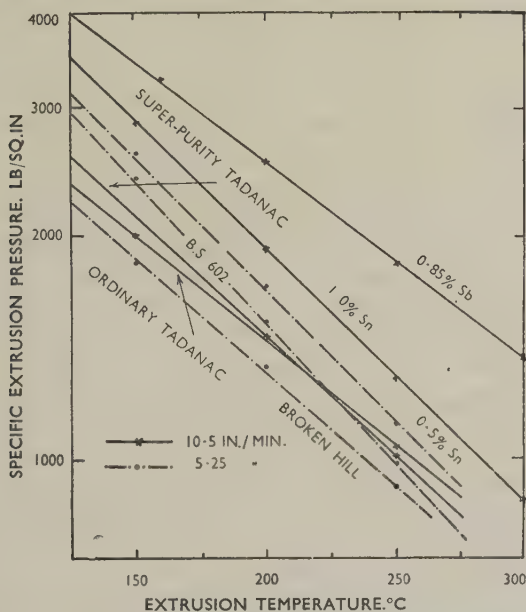


FIG. 6.—Relationship between Specific Extrusion Pressure and Temperature for Constant Rate of Extrusion.

by small amounts of chemical lead and alloy sheet for specific service conditions. It is usual to classify the various alloys under three headings; the so-called Type *A* chemical lead, which is a highly pure lead used extensively in chemical plant; Type *B* chemical lead, which is pure lead with any specific addition (usually copper) demanded by the consumer; and ordinary lead which conforms in general to the B.S. 602 specification.

With the exception of antimonial alloys, the materials are cast into horizontal slabs, approximately 8×8 ft. \times 6–8 in. thick, and broken-down in the mill at the highest temperature at which the slab may be raised and placed on the mill bed, usually at about 200° C. The slab

is broken-down in reversing, two-high mills to about 1 in. thickness in approximately 20 passes, cut into suitable lengths, and cold rolled to finished thickness in a further 20 passes. Antimonial slabs are often cast in vertical moulds, employing bottom pouring, and are poured at as low a temperature as possible, depending upon composition, in order to minimize segregation. The as-cast slabs of 6–8% antimony alloys, the composition which is usually called for, are notoriously brittle owing to segregation of antimony-rich material at the grain boundaries and care must be exercised in keeping rolling temperatures below 200° C. to avoid hot shortness. It is important in the case of antimony alloys to destroy this brittle as-cast structure as completely as possible, and as much as 95% reduction is often necessary to effect this.

Type *A* chemical lead finishes on the mill bed with relatively small grain-size but in an unstable condition, such that small strains of the order of $\frac{1}{2}$ –2% are sufficient to cause the development of large grains. Strains of 2% or more generally result in complete recrystallization of the product from a large number of nuclei and produce relatively stable structures of medium grain-size. The strains induced in coiling the sheet subsequent to rolling are of the order of 2% and, unless sufficiently small coiling rolls are employed, this critical straining often occurs and large grains develop to the detriment of the general mechanical properties of the sheet.

In the case of Type *B* chemical lead and other lead alloys, it would seem that structurally the sheet finishes on the mill bed in a relatively stable condition of small grain-size or else completely recrystallizes after coiling, which results in general in a medium-grain-sized structure. The final draft and the coiling operation are therefore of importance in determining the ultimate structure of the sheet, and light, final passes are avoided as being likely to leave this structure in the highly unstable condition which favours the development of large grain on coiling. The factor which to a large extent determines the reductions employed is the necessity of keeping the sheet flat. Too small a pinch will tend to extrude the metal from the roll centres towards the edges, and too large a draft will result in the opposite effect and the metal will be squeezed to the centre. The optimum draft, therefore, is determined not by considerations of the metal structures or properties, but in large part by the roll camber employed and the resistance to deformation of the alloy being rolled.

V.—IMPACT EXTRUSION OF LEAD.

The use of the softer metals in the development of impact extrusion as an industrially important means of forming, and its subsequent

application to other non-ferrous materials, is similar in many respects to the important rôle which they played in the ultimate development of the hot-extrusion method of preparing metals in wrought form. Collapsible lead tubes were being manufactured on an industrial scale as long ago as the latter half of the last century, but it is only comparatively recently that the method of impact extrusion has been used to any great extent to form the harder metals. The significance of the process when applied to lead is still much as it was over 50 years ago, and lies in the ready means it affords of producing thin-walled collapsible tubes which are used extensively in the packing of toilet preparations and other commodities.

The process consists in placing a cold slug of metal in a shallow die and subjecting it to a sudden blow by a punch which causes the metal to flow up through the annular space between the punch and die and over the reduced shank of the punch. The rapid deformation causes considerable temperature rise in the metal and the process is thus a hot-working operation in the case of lead.

The greater part of the output of collapsible lead tubes in this country is of a tin-lined or tin-coated lead, the tin serving either as a protective inner coating or as an outer flash which enhances the appearance of the tube. Tubes of this type are extruded from tin-coated lead slugs punched from a sandwich sheet which is prepared by rolling lead slabs between a jacket of two tin/lead plates. The tin/lead jacket plates are prepared separately by rolling tin sheet and lead slabs together through a heavy draft, the two-stage preparation process permitting closer control over the final tin thickness and ensuring a good pressure weld between the two.

Good lubrication of the slug and working faces of the press tools is of extreme importance in promoting a uniform flow of metal, and it is usual to add a lubricant to the slugs during barrelling, an operation which is carried out before extrusion in order to remove the fins resulting from the punching. In the case of lead, this lubricant may be an oil or soap compound in either the liquid or finely divided solid state.

A 50-ton press, with automatic feed and stripping devices, will press tubes from these slugs at a rate of 50–80/min., the actual working operation on the slug being completed in something like $\frac{1}{10}$ th sec. This rapid deformation is accompanied by a considerable temperature rise of the slug metal and products may leave the press at temperatures above 100° C.

Because the temperature of the metal is rising, its resistance to deformation is continuously changing, and this consideration, together with the fact that the flow is not a simple inverted type but is con-

siderably influenced by surface friction, leads to the rejection of the possibility of a simple exponential relationship existing between punch-load and reduction, as has been found for the inverted extrusion of metals under laboratory conditions. Hanes⁴ has recently given some of the results of his investigations into the behaviour of several light alloys when impact extruded and reproduces punch load—reduction curves which are not reducible to a simple exponential form. A knowledge of such relationships is of considerable importance to the engineer, particularly with reference to the harder metals and alloys, where tools may be working under extreme conditions of loading.

Very little has been published about the metallurgical factors affecting the impact extrusion of lead and lead alloys.

ACKNOWLEDGEMENTS.

The author has had the benefit of much advice from representatives of the lead pipe, foil, and cable industries in the preparation of this paper, and his thanks are due to all those who have helped in this way.

He is also indebted to the Director and Council of the British Non-Ferrous Metals Research Association for permission to publish the paper.

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THE ROLLING OF ZINC AND ZINC-RICH ALLOYS.* 1232

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SYNOPSIS.

The methods used for the production of zinc and zinc alloy sheet and strip are described, and brief reference is made to the manufacture of other rolled forms. The metallurgical problems associated with the rolling operations are discussed, and the effect of rolling on the mechanical properties of the product is examined.

I.—INTRODUCTION.

THE rolling of zinc and the associated metallurgical problems have not received a great deal of mention in the technical literature of this country during recent years. This is not surprising since the tonnages rolled are not large compared with some of the other non-ferrous metals and the applications of the products, while important, are specialized and well established but not numerous. Examples are the manufacture of lithographic and other printing plates, battery cans, roofing sheet, and sacrificial protection plates for ships' boilers and hulls, while a more recent use is as an interleaving in motor-car springs to provide both corrosion-protection and lubrication. The manufacture of blanking dies presents an expanding outlet for zinc alloy sheet, the alloying elements being aluminium and copper.

Zinc rolling is, however, a subject of considerable metallurgical interest. Unlike the majority of the common metals, zinc belongs to the hexagonal crystallographic group and recrystallizes at or near room temperature. The effect of rolling on mechanical properties is therefore different from that found in most other metals, and there is no clear line of demarcation between hot and cold rolling. All commercial rolling operations can, in fact, be described as hot rolling as far as unalloyed zinc is concerned, but, for convenience, "hot rolling" is used in this paper to describe work performed above about 150° C., while "cold rolling" denotes work performed near room temperature.

The object of the paper is to describe the various rolling operations

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used for the production of sheet, strip, foil, and rod in zinc and zinc-rich alloys and to examine the metallurgical problems involved in these methods of manufacture.

II.—SHEET AND STRIP PRODUCTION.

1. *Casting of Rolling Slabs.*

Zinc is normally melted either in gas-fired reverberatory furnaces of up to 100 tons' capacity or in low-frequency induction furnaces, the capacity in the latter case being of the order of a few tons. It is usual to blend several grades of metal to obtain rolling slabs of constant composition. The metal temperature is maintained below 500° C. to minimize loss by oxidation and volatilization, and since a dipping ladle is used to carry the metal to the moulds the actual pouring temperature is usually about 440° C.

The greater proportion of rolling slabs are cast in open-top horizontal moulds although certain firms favour one or other variety of vertical mould. The semi-continuous method of casting has been tried but does not appear to have been widely adopted, while of the other possible methods of slab production a vacuum-casting method has in recent years been used with success in Germany.

Open-top horizontal moulds are usually of cast iron and mounted on revolving tables. The size of slab produced can be controlled by inserting liners to reduce the length or width and by varying the height of the metal poured. The mould temperature is regulated either by water sprays directed upwards from below or by cooling fins extending from the base into water flowing at a predetermined rate. A mould temperature of 100°–120° C. appears to be the most satisfactory, higher temperatures promoting the formation on the surface of the slab of oxide films which, since slabs are not normally scalped, might produce discoloration or other defects on the surface of the finished sheet. An electrically heated flat cover is sometimes placed over the mould with the object of minimizing surface shrinkage, the elimination of which is one of the main problems associated with this method of casting.

Vertical moulds, where used, are mounted on trunnions hinged either at the side or bottom to facilitate ejection of the slab and may or may not be water cooled. At the beginning of pouring the mould is tilted and gradually brought to the vertical as the level of the metal rises. A feeder-head is sometimes fitted to the mould, but a considerable length has to be cropped from the top of the slab, owing to unsoundness, even when this device is incorporated. The complexity of the vertical mould as compared with the horizontal type, together with the expense

of installation of the cropping shears and the remelting of the crop ends, adds considerably to the cost of rolling slabs when this method of production is used.

In the vacuum-casting process employed in Germany during recent years the mould, of rectangular cross-section and fitted with cooling fins at the sides, is lowered over the well of a melting furnace holding the metal. The top of the mould is connected to a vacuum pump by means of a flexible pipe and when the bottom is in position below the metal surface a controlled vacuum is applied until the mould is full. The bottom of the mould tapers to a much smaller section and the slab is ejected through the top.

Zinc rolling slabs have been cast quite successfully by semi-continuous casting methods, but since satisfactory products can be obtained by the use of less expensive equipment the semi-continuous system is not normally employed.

Reheating.

The slabs are reheated at a temperature of 140°–200° C. for 5–24 hr., depending on the composition of the material. The presence of much cadmium or copper results in a cored structure in the casting and the higher temperature and longer time are then necessary to take these elements into solution and render the structure homogeneous.

Reheating furnaces may be of simple design or may be of the belt-conveyor type, the latter variety being more common in highly mechanized mills running to a strict production schedule. When working with metal of fairly high purity reheating is sometimes dispensed with altogether. The slabs are stacked after casting, allowed to cool to the desired temperature, and sent direct to the roughing mill.

2. The Rolling of Sheet and Strip.

Two methods of production are in use at the present time, pack and strip rolling. The older pack-rolling system possesses the advantage of wide adaptability with regard to size of sheet, quantity, &c., but, as in other branches of the metallurgical industry, an increasing tonnage of zinc is now being handled by strip mills. Sheets up to 60 in. wide can be produced by the older system, while at present the width of strip is limited to about 30 in.

Pack Rolling.

Plant, mill lay-out, and production methods follow a similar pattern in all countries, details, of course, being varied to suit local conditions. The system outlined below is typical.

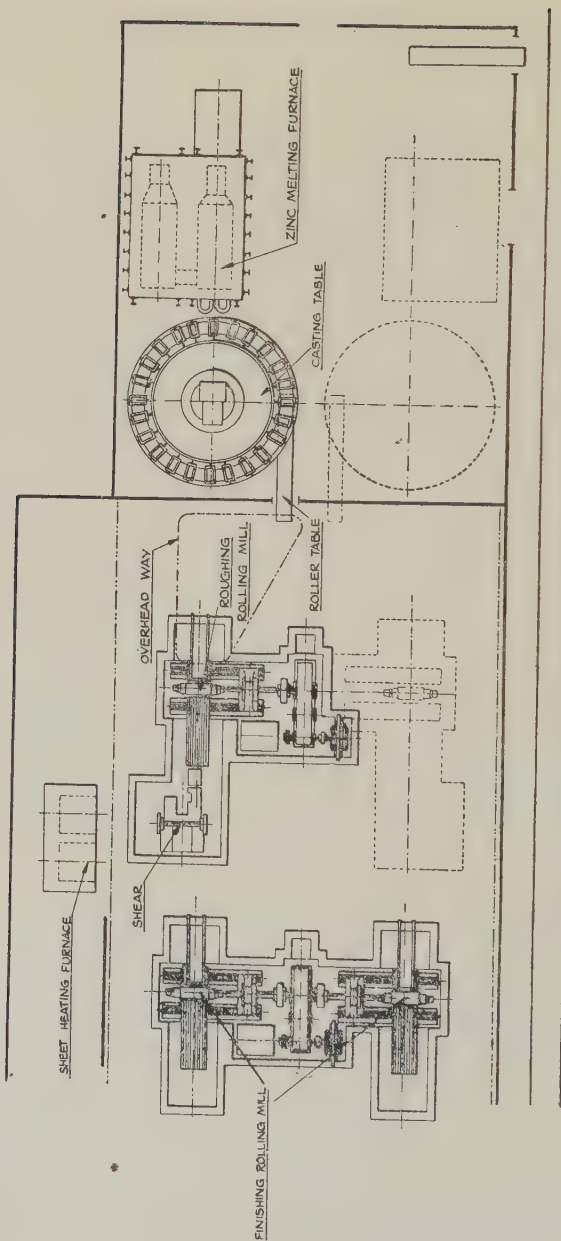


FIG. 3 (a).—Typical Lay-Out of Zinc Sheet Mill (see also Fig. 3 (b)).

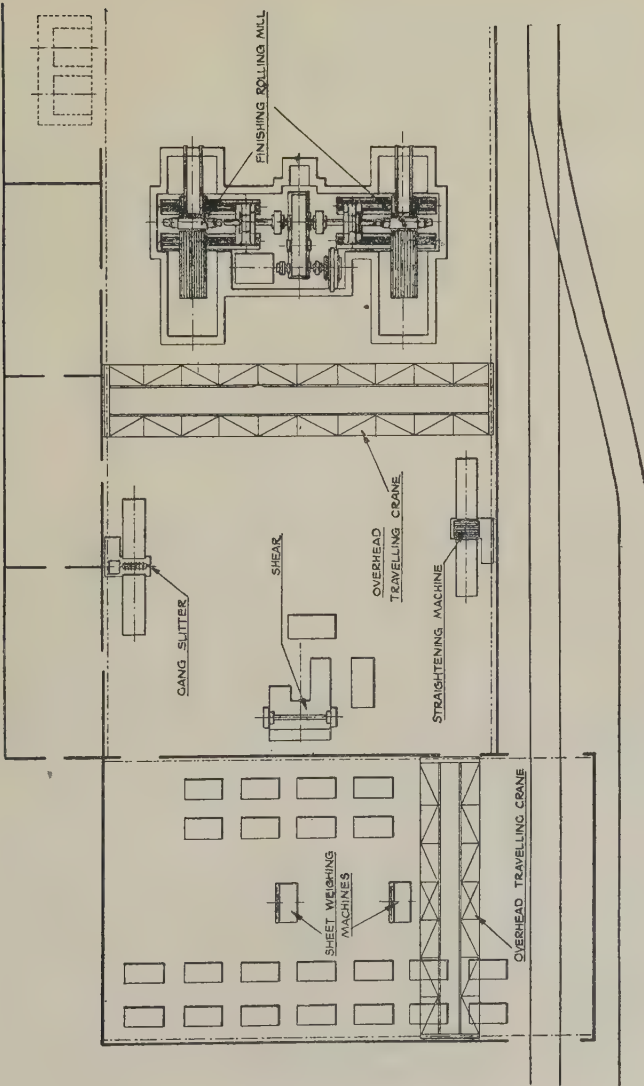


FIG. 3 (b).—Typical Lay-Out of Zinc Sheet Mill (see also Fig. 3 (a)).

The dimensions of the slab are governed by the size of sheet required, but the thickness is generally $1\frac{3}{4}$ –2 in. Two-high mills are used for breaking-down, the rolls being 18–24 in. in dia. and up to 66 in. wide, with a peripheral speed of 150–250 ft./min. As stated earlier, the slab temperature varies with composition, but 150° C. would be an average figure for good-quality zinc. The slab is first rolled to increase its length to the required width of the hot-rolled sheet, allowance being made for edge trimming, then turned through 90° and rolled to the required thickness. To reduce the thickness from 2 in. to about 0.060 in. thirteen to seventeen passes are required, the sheet being doubled for the last few passes to facilitate handling and to save time. A lubricant is applied to the sheet surface, mixtures of tallow and paraffin wax being commonly used for the purpose. The thickness at which roughing stops varies with the gauge of the finished sheet, and when the desired thickness is obtained the strip is edge trimmed and cut into sheets of suitable size which are assembled into packs of from 15 to 30 sheets, the actual number depending on the gauge required in the finished sheet.

Cold Rolling.

The mills are usually two-high with rolls of chill-cast iron or alloy steel, 22 to 26 in. in dia., and up to 80 in. wide. Rolling speed varies with the power and size of the mill and may be as low as 30 ft./min. The pack is rolled at right angles to the direction of roughing and after about every fourth pass is split in such a way that when rolling is completed each side of each sheet has been against the rolls at least once. This shuffling equalizes sheet thickness and produces a better surface finish. Reduction per pass is light, the last few passes merely serving to iron out the sheets. Accuracy of gauge cannot be expected from pack rolling and a tolerance of $\pm 6\%$ in thickness is allowed.

Mill Design and Lay-Out.

A detailed discussion of this aspect is outside the scope of the present paper. Figs. 1 and 2 (Plate LXXVII) are, however, included to show the general arrangements of roughing and finishing mills, respectively, while a typical lay-out of a sheet mill is illustrated in Fig. 3.

Strip Rolling.

During the past twenty years, particularly in the United States and Germany, an increasing quantity of zinc has been rolled in strip mills. Procedure varies somewhat but the two systems outlined below illustrate the methods generally adopted.

Example (1).¹ The slab dimensions are $700 \times 1300 \times 83$ mm.

(28 × 52 × 3.3 in.), their weight 530 kg. (1200 lb.), and the rolls are 900 mm. wide and 450 mm. in dia. The slabs, before cooling, are broken-down to plates 23–25 mm. thick. The following reductions are taken :

4 reductions of	4 mm. = 16 mm.
2 " "	12 mm. = 24 mm.
1 " "	8 mm. = 8 mm.
1 " "	6 mm. = 6 mm.
1 " "	4 mm. = 4 mm.
<hr/>	
Total reduction = 58 mm.	
<hr/>	

The broken-down plates, 25 mm. thick and trimmed to a width of 670 mm., are soaked at 60° C. and then rolled to strip, the following reductions being taken :

19 reductions of 1 mm. reducing strip to 5 mm. thickness.					
3	"	0.75	"	"	2.75
1	"	0.65	"	"	2.10
1	"	0.60	"	"	1.50
1	"	0.50	"	"	1.0
1	"	0.45	"	"	0.55
1	"	0.30	"	"	0.25

Example (2). The two-high roughing mill, with rolls 18 in. in dia. by 30 in. face, reduces a slab 2 in. thick to strip of 0.070 in. gauge in five to eight passes. A drive of about 250 H.P. would be required to handle work of these dimensions.

The two-high, non-reversing finishing mill is of approximately the same power, but the roll diameter is 15 in. The rolls are heated on the exit side by gas burners. The strip is started cold, but owing to the warmed rolls and the heat generated by rolling it rapidly attains a temperature of about 100° C. This results in a strip in "dead soft" condition, but if increased rigidity is required in the final product the last few passes are taken with rolls that are literally cold. Five or six passes are needed to reduce the gauge from 0.070 to 0.020 in. Batches of from 8 to 12 coils are passed through the mill before resetting the rolls for the next reduction.

A description has appeared,² of a highly mechanized strip mill where batches of up to 25 slabs in the roughing mill and 75 coils in the finishing mill are handled simultaneously. This may indicate the trend in zinc strip-mill practice, but it is doubtful whether many mills work to such a complex schedule at the present time.

3. General Remarks.

Casting.

Zinc rolling slabs are not normally scalped. This operation, common in non-ferrous rolling practice, is omitted mainly to reduce production

costs, the sheet imperfection associated with surface defects in the slab not being very prominent. In addition, it has been found that scalping tends to open up fine shrinkage cracks which otherwise would probably weld up during hot rolling.

In this connection may be mentioned an additional advantage of open-top horizontal moulds as compared with other designs. A minimum restraint to shrinkage is afforded with this type of mould and consequently the risk of surface cracking during cooling is minimized.

Rolling.

During recent years the trend has been towards high-speed rolling, owing to the economic advantages of the type of unit involved, and modern strip mills can now rough at 250 ft./min., finishing speeds being in the order of 500–550 ft./min. Experiments with speeds of 1000 ft./min. have been made with some success, but attendant difficulties are considerable and such speeds of rolling have not been adopted.

Although zinc is one of the softer materials, zinc strip mills require almost the same power to drive as does a steel-rolling mill making the same reductions on the same size strip. While zinc deforms readily under slowly applied loads of moderate dimensions its resistance to deformation increases rapidly with increased rate of loading.

There appears to be some divergence of opinion regarding the most suitable material for the construction of rolls. For roughing, alloy steel possesses greater shock resistance, but chill-cast iron is often used and seems to give satisfactory service. Steel rolls are more desirable in finishing mills, particularly for the last pass or two, but chill-cast iron is less susceptible to the change of dimensions with temperature which causes "ballooning".

The Rolling of Zinc Foil.

During recent years substantial tonnages of zinc foil have been produced in Germany and lesser quantities in the United Kingdom and the United States. The Germans used high-purity zinc for the purpose, while in this country and the United States high-purity zinc containing small percentages of manganese has often been used. This addition of manganese was found necessary in order to suppress recrystallization and grain growth of the exaggerated type, with the resultant embrittlement of the sheet, which was found to take place when high-purity zinc was used for foil production.

General experience indicates that a satisfactory product can be

obtained from mills designed for aluminium foil rolling, and the rolling technique is very similar although, owing to the greater resistance to deformation of zinc, certain modifications are necessary. The roll camber is increased, a greater number of passes are necessary for similar reductions, and the tension in the strip requires more critical control. The last pass is usually taken with the foil doubled, two coils being fed to the mill simultaneously. This results in a foil with one side bright and the other matt, which appears to be desirable for most applications.

Rolled Zinc Bar.

Zinc is rolled into round bar as a preliminary or intermediate stage in the production of wire. Billets about 6 in. in dia. and 36 in. long are cast, rolled through the usual series of diamond, oval, square, round, &c., sections to rod of about 0.25 in. dia. and then drawn down to wire of the required gauge. An alternative method is to extrude rod of 0.50–0.75 in. dia., which is then rolled to about 0.25 in. dia. before drawing.

4. Other Methods of Zinc Rolling.

Hazelett Process.

This process for the production of metal strip was patented in America in 1932 and zinc strip was produced experimentally, although there is no record of the method having been used commercially for the purpose. However, since it is of interest both from the point of view of continuous casting and strip rolling, a brief description is given.

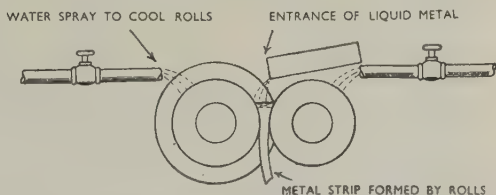


FIG. 4.—Essentials of Hazelett Mill.

The arrangement is shown diagrammatically in Fig. 4. Molten metal is poured between two slowly rotating rolls, one of which is flanged, and the speed of rotation and degree of artificial cooling are controlled so that a layer of metal solidifies on the rolls and emerges at the underside as a continuous strip. The strip is passed to conventional mills for reduction to the required gauge. Considerable operational difficulties were encountered, but sufficient progress was made in America to enable brass strip to be manufactured in this type of mill on a commercial basis. The main difficulty encountered during the experiments with zinc was the very marked directional properties of the strip produced.

Electrolytic Process.

Zinc strip of thickness up to 0.022 in. has been manufactured by electrodeposition of the metal on a rotating drum, the stationary anode, surrounded by an absorbent material holding the electrolyte, being held against the face of the drum under light pressure. The strip is peeled off the drum, passed through a bath of the electrolyte to increase its thickness, and then lightly rolled to improve its surface condition.

The process is described in German Patent No. 586,490, and experimental quantities of sheet zinc were produced in this country in about 1934. It is doubtful, however, whether such a process has ever been used commercially for the production of zinc strip.

III.—METALLURGICAL CONSIDERATIONS.

1. *Hot Rolling.*

In the cast state zinc is coarsely crystalline, large columnar crystals extending from the cooling surfaces deep into the casting, and with slabs of up to 2 in. in thickness the crystals growing from opposite faces may meet at the centre, there being no zone of equi-axial grain. Such a structure, being mechanically weak, is undesirable in rolling slabs and much work has been done with a view to obtaining grain refinement. Control of cooling rate, inoculation, stirring, addition of alloying elements, are among the methods that have been examined.

None has been particularly successful except the last. Recent work by Anderson, Boyle, and Ramsey³ has shown that the addition of 0.1–0.2% titanium to high-purity zinc results in marked grain refinement. Such additions have a considerable effect upon the mechanical properties of the sheet subsequently produced, which will be discussed in a later Section, but it is not clear whether this method of grain refinement is being used commercially.

Zinc crystallizes in the hexagonal system, and Edmunds,⁴ investigating orientation in cast ingots, reported the hexagonal axis lying approximately at right angles to the direction of growth of the columnar crystals, with the basal (0001) plane parallel to the direction of growth.

This columnar structure comprising crystals with strongly preferred orientation results in the mechanical properties of cast slabs being markedly directional. Northcott⁵ obtained ultimate stress figures of approximately 3.4 and 1.0 tons/in.², respectively, for specimens cut parallel to and normal to the direction of growth of columnar crystals in cast zinc. Figures for elongation were, respectively, 4.5 and 1.5%. Notched-bar impact values for test-pieces with the notch parallel to and normal to the direction of growth were 5.0 and 5.8 ft.-lb., respec-

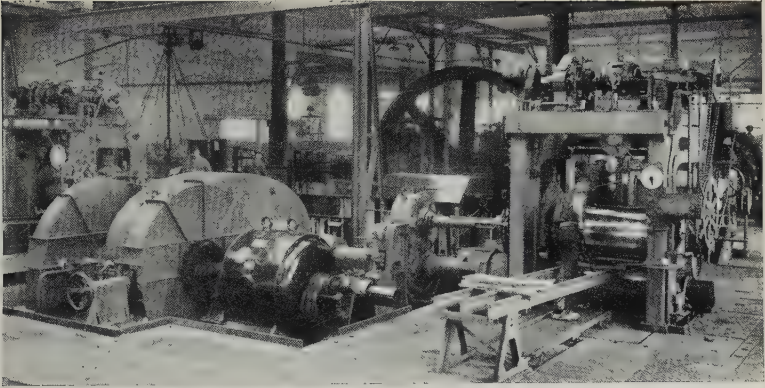


FIG. 1.—Hot-Rolling Mill for Zinc.

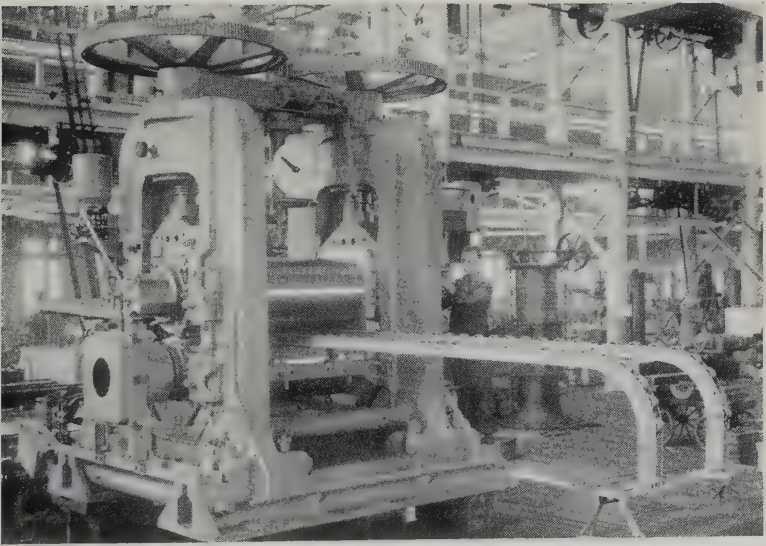


FIG. 2.—Cold-Rolling Mill for Zinc.

tively, at 20° C., a difference of 16%; while at higher temperatures, the difference increased greatly, being 62% (46 and 75 ft.-lb., respectively) at 100° C. and 43% (49 and 70 ft.-lb., respectively) at 150° C. It appears, therefore, that the resistance to fracture of zinc crystals across the basal (0001) plane is low, while across the prismatic (10 $\bar{1}$ 0) plane it is considerably greater.

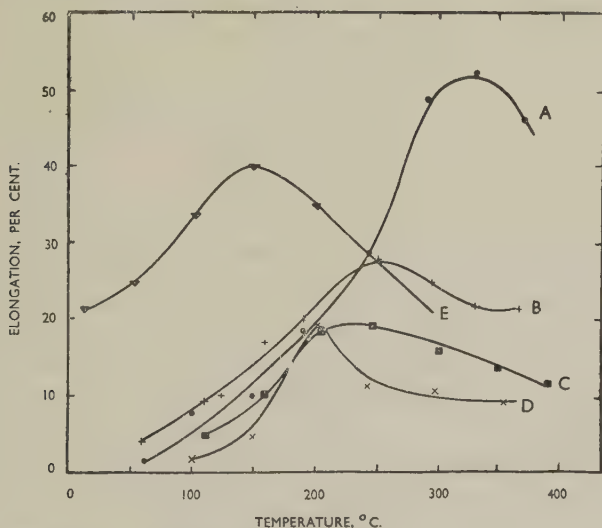


FIG. 5.—Effect of Hot-Rolling Temperature and Purity on Percentage Elongation.

KEY.
 A. Zinc as cast, purity 99.994%.
 B. Zinc as cast, purity 99.988%.
 C. Zinc as cast, purity 99.958%.
 D. Zinc as cast, purity 99.974%.
 E. Zinc hot rolled, purity 99.00%.

The deformation of zinc crystals will be discussed later, but it may be stated here that deformation normally takes place in two directions only, slip along the basal plane and twinning across the pyramidal plane. (It is possible that slip may also take place along the prismatic and pyramidal planes.) The initial stage of breaking-down is therefore critical, and should consist of light reductions taken, if possible, in two directions. Heavy reductions would probably lead to excessive cracking since, with a structure comprising large crystals of which only a limited number are favourably oriented for slip, the possibility of avoiding the building up of excessive stress across the weak basal plane is remote.

The toughness and plasticity of cast zinc increases rapidly with increasing temperature. Curves A-E, Fig. 5, illustrate the variation

with temperature of the mechanical properties of five grades of zinc, while the impact figures quoted above indicate a maximum resistance to shock-loading between 100°–150° C. Curve *E*, taken from a paper by Burkhardt,⁶ shows that the plasticity of zinc containing approximately 1% lead reaches a maximum at about 150° C., while above and below this temperature the plasticity is much lower; the tensile strength at the temperature of maximum plasticity remains reasonably high. Curves *A–D*, due to Evans and Harrison,⁷ illustrate the variation of plasticity for four zincs of higher purity. From these data it appears that high-purity zinc may be hot worked over a wide temperature range and that high plasticity over a limited temperature range is associated with high impurity content. This is in accordance with the experience of commercial zinc rollers.

Confirmation of the first point has been obtained by Northcott.⁵ Experimenting with zinc of 99.994% purity, he found that slabs of 2 in. thickness could be hot rolled to 0.10 in. strip over the temperature range 350°–100° C. The second point is discussed in a later Section (see p. 573).

As stated above, deformation of the hexagonal lattice takes place mainly in two directions, slip parallel to the basal plane and twinning across the pyramidal plane. At the temperature of hot working, the strain induced by deformation results in spontaneous recrystallization with the formation of a greatly increased number of smaller crystals with random orientation. With such a structure there will always be available a large number of crystals with basal planes favourably oriented for further deformation. Slip parallel to the basal plane will therefore take place at low stress, thus relieving any stress normal to adjacent basal planes, and under these conditions the metal may be cold worked. It is necessary therefore that hot work be continued to the point where recrystallization of the metal is complete. Data on the amount of hot reduction required to bring about this condition is also given in Northcott's comprehensive paper.⁵ Slabs of high-purity zinc (99.994%) were given hot reductions of from 5 to 80% and then cold rolled to the point where cracks, if any, appeared. From the figures obtained, it appears that 40–50% hot reduction is necessary before cold rolling can safely be attempted.

2. Cold Rolling.

Deformation of the Hexagonal Zinc Lattice.

Deformation of metallic crystals takes place normally by the slipping or gliding of blocks parallel to certain crystallographic planes, the lattices of adjacent blocks, however, retaining their original orienta-

tion except for slight distortion. In cubic metals there are 12 possible planes in which slip may take place, but only one such plane is normally available in metals crystallizing in the hexagonal system (in which class zinc falls), namely, the basal (0001) plane. The crystal structure of zinc is illustrated diagrammatically in Fig. 6. It is possible that at high temperatures deformation may also take place by slip along the pyramidal ($10\bar{1}2$) and prismatic ($10\bar{1}0$) planes, but it is unlikely that these planes come into action at lower temperatures.

In addition to basal slip, the zinc crystals may also deform by twinning across the pyramidal plane, as shown by the investigations of Mathewson and Phillips.⁸ The process (in a simplified picture) is as follows. As basal slip proceeds the impeding forces increase and a correspondingly greater stress is required to cause slip to continue. Lattice distortion consequently becomes greater and if, across the pyramidal plane, the atoms on one side are moved, by displacements or restricted slip, into certain positions (or near to them), the forces of recrystallization bring about re-orientation and stabilize the lattice in this new position, so that the atoms occupy positions that are the mirror images of those in the original lattice reflected across the pyramidal plane. Twinning itself does not result in much deformation (a reduction of 6.75% in terms of the thickness perpendicular to the basal plane has been calculated⁸), but the re-orientation results in a new set of basal planes becoming available, at an angle of 94° to the original, on which further deformation can proceed.

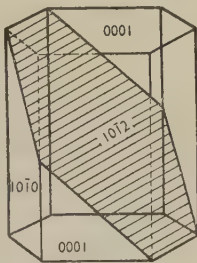


FIG. 6.—Crystal Structure of Zinc.

Deformation of Zinc Single Crystals.

Research on this subject has been carried out by a number of investigators with a view to elucidating the phenomena associated with the hot and cold working of zinc.

A zinc single crystal, if favourably oriented, when tested in tension begins to elongate at a very low load. Hoyt⁹ states that a shear stress of 125 g./mm.² along the basal plane is sufficient to start slip.

The crystal, if originally cylindrical, draws down to a strip of elliptical cross-section, the resistance to slip increases rapidly, and the angle between the traces on the surface of slip planes and the direction of load becomes less. When this angle becomes about 20° either fracture or further elongation may occur, the major axis of the ellipse decreasing and the crystal drawing down to a thread of cylindrical cross-section.

An elongation of 300% may be obtained, the shear-stress at fracture being about 7000 g./mm.² Mathewson¹⁰ stated that the original elongation was due to basal slip, the increase in strength being due to twinning (thus forming basal planes unfavourably oriented for slip) and lattice distortion. The second stage of elongation, called "after-elongation", is due to slip on the secondary basal planes formed by twinning.

One other property of zinc single crystals must be mentioned. Mathewson and Phillips⁸ observed that the scleroscope hardness figure varied with orientation, being 10–11 when the basal plane was parallel to, or at a very small angle to, the test surface and decreasing to between 6 and 7 as this angle increased.

Effect of Rolling on Mechanical Properties of Zinc.

The majority of the common metals crystallize in one or other of the cubic systems, and it is well known that cold work results in an increase in hardness, tensile strength, and yield point, while the elongation, reduction in area, bending capacity—in short, the toughness—decrease. Earlier investigations on the effect of cold work on the mechanical properties of zinc had provided conflicting evidence, but recent research has clarified the matter to a considerable extent.

Unlike most metals zinc cannot be hardened to any appreciable extent by cold work, the reverse, in fact, being true. Chadwick,¹¹ working with zinc of 99.988% purity, obtained diamond pyramid and scleroscope hardness values for zinc sheet that had received cold reductions of up to 80%. A maximum diamond pyramid value was obtained at about 30% reduction, after which the material became progressively softer with increasing cold reduction. Scleroscope hardness figures increased continuously with increasing cold reduction. Storage at room temperature for a month resulted in the diamond pyramid value increasing to a figure slightly above that of the original material, while the scleroscope value decreased to a figure also slightly above that at the start. The curves obtained by Chadwick are shown in Fig. 7. Results for ultimate strength, were also correlated with percentage cold reduction by Chadwick, the curves obtained being reproduced in Fig. 8. The improvement in mechanical properties produced by limited cold reduction is not permanent; the values obtained after 1 month at room temperature are near to or below those of the original material.

In the same Figure are shown curves⁶ correlating ultimate stress and percentage elongation with percentage reduction for commercial zinc containing 1% lead. The initial 40% reduction was, in this case, carried out at the normal hot-working temperature, only that portion of the

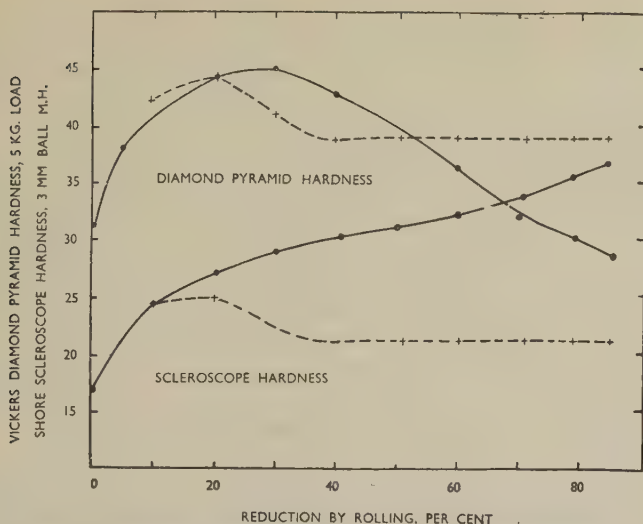


FIG. 7.—Effect of Cold Rolling on the Hardness of Zinc Strip.

Continuous line = as rolled.
Broken line = after 1 month.

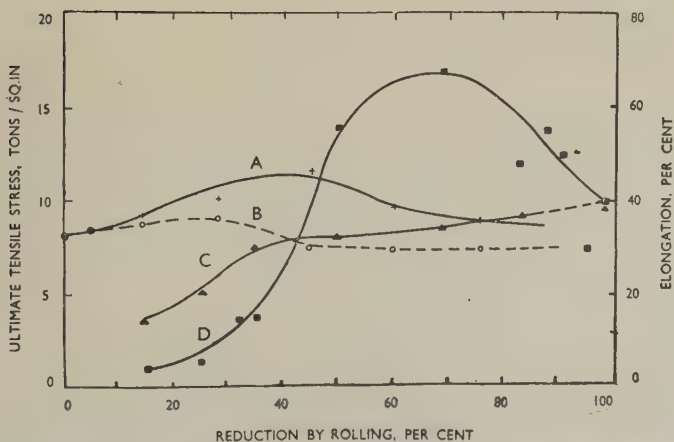


FIG. 8.—Effect of Cold Rolling on Ultimate Strength and Percentage Elongation of Zinc Strip.

KEY.

- A. Electrolytic zinc, as rolled (U.T.S.).
- B. Electrolytic zinc, after 1 month (U.T.S.).
- C. Commercial zinc (U.T.S.).
- D. Commercial zinc (elongation).

curve between 40 and 95% representing the changes brought about by cold rolling. Working with a somewhat less pure grade of zinc than that used by Chadwick (99.954%), Ingall,¹² in 1921, obtained a maximum Brinell hardness value at about 90% reduction, after which it decreased rapidly. His figures for percentage elongation and reduction in area also showed a maximum at 90% reduction, while the ultimate stress and yield point increased up to 96% reduction.

The directional properties of rolled zinc are also well illustrated by Ingall's work. His figures, the more important of which are given in Table I, indicate that after hot rolling ductility is markedly greater in the direction of rolling than in the transverse direction, while the ultimate stress is slightly higher in the latter direction. At about 90% reduction this difference in ductility disappears, while the directional ratio of ultimate stress remains unaltered.

TABLE I.—*Tensile Properties of Hot-Rolled Zinc (Ingall¹²).*

Reduction, % *				Ultimate Tensile Stress, tons/in. ²	Elongation, %	Reduction of Area, %
77.5	Longitudinal	.	.	8.85	84	91
	Transverse	.	.	9.48	26	22
85.8	Longitudinal	.	.	8.58	77	83
	Transverse	.	.	9.82	30	23
92.3	Longitudinal	.	.	11.70	52	83
	Transverse	.	.	13.00	50	81

* The percentage reduction is expressed in terms of the thickness of the original slab. It appears that hot rolling was taken to about 70% reduction.

The effect of cold reduction on the creep strength of zinc is most marked. Using a load of 5000 lb. and reporting the rate of creep in in./in./min. Chadwick¹¹ obtained a figure ($\times 10^{-5}$) of 1.7 for the material in the softened condition, which increased to 100 after 75% cold reduction; while after storage at room temperature for 1 month the figure for this cold-rolled material fell to 0.43.

Since zinc is little hardened by cold work intermediate softening is rarely necessary, but if it is required a further hot-working operation appears to be the only satisfactory method of bringing the metal to a state suitable for further cold deformation. Annealing at any temperature is of little value in this respect and may produce the reverse effect. Ingall¹² reports an increase in the Brinell hardness of zinc sheet when annealed at temperatures below 150° C., while annealing the material above 150° C. results in a marked decline in plasticity as shown by elongation and reduction-of-area figures. Burkhardt⁶ reports a similar

trend with a zinc of electrolytic purity, the elongation figure in this case declining to about 8%. Similar results have been reported by other investigators ¹³ using zinc of lesser purity.

The alteration of mechanical properties on annealing can be associated with change of structure. It has been shown ^{13, 14} that annealing at progressively higher temperatures results in marked coarsening of the structure, the rate of grain growth increasing with increasing degree of cold work.

The effect of rolling on grain orientation has been investigated. Caglioti and Sachs ¹⁵ reported that the hexagonal axis is found most frequently inclined at an angle of 20°–25° towards the rolling direction, this orientation being largely retained after recrystallization. The influence of this orientation on the properties of the sheet is discussed on p. 575.

3. Effect of Impurities on Rolling Properties.

The impurities normally present in zinc are lead, iron, cadmium, with much smaller amounts of copper, arsenic, and possibly tin.

The solubility of iron in zinc is about 0.001%, and quantities much in excess of this figure form an intermetallic compound which, being finely dispersed, increases hardness and reduces ductility. This leads to excessive edge cracking during hot rolling, and consequently the iron content of zinc intended for rolling is limited to about 0.02%.

The presence of lead appears to have little effect on the rolling properties of zinc at the usual temperature and up to 1.25% can be tolerated.

The tin content must be of a very low order. The metal crumbles during hot rolling when 0.004% of this impurity is present, while even 0.002% causes an undesirable amount of edge cracking. The solubility of tin in zinc is very low, and it is probable that with the other insoluble impurities present it forms an intercrystalline envelope of a eutectic, the melting point of which is near the temperature of hot rolling.

The effect of arsenic on the rolling properties of zinc is similar to that of iron. Cadmium has a considerable solid solubility in zinc and is known to exert a pronounced influence on the work-hardening properties of the sheet. If a "dead soft" sheet is required the cadmium content is limited to about 0.020%. It has been shown ¹¹ that the extent and permanence of the increased hardness obtained is influenced to a considerable extent by the amount of rolling, optimum properties being obtained at about 30% cold reduction. Further reduction results in a progressive softening of the sheet. The increased hardness obtained

by cold rolling in zinc containing cadmium decreases with time of ageing at room temperature.^{11, 16}

Magnesium and titanium are not impurities naturally occurring in zinc, but for convenience the effect of their presence in small quantities is included in this Section.

The presence of 0.005–0.010% magnesium considerably increases the hardness and ultimate strength of cold-rolled zinc, the hardness increasing and the ultimate strength decreasing on subsequent ageing at room temperature. Resistance to creep is also greatly increased (as compared with pure zinc), but the improvement is not permanent.¹¹

The reverse effect with respect to creep-resistance has been reported³ when about 0.1% titanium is present in zinc. Hot rolling results in a material with greatly increased resistance to creep, but subsequent cold rolling reduces this desirable property to a very modest level, while annealing after cold work restores to a large extent the improved creep-strength of the material.

4. *Discussion.*

It is clear from the foregoing that zinc is distinctly individualistic in its rolling behaviour owing to a combination of the following characteristics :

- (a) Hexagonal lattice.
- (b) Recrystallization temperature in the range of normal "cold" rolling temperatures.
- (c) Specific effects of impurities.

Thus the rolling behaviour combines the effects found in magnesium (hexagonal lattice) and lead (low recrystallization temperature).

The hexagonal lattice encourages the formation of columnar crystals in the cast slab which, in the horizontally cast slab, are not generally favourably oriented for slip, hence the necessity for particular care in the breaking-down stage.

In the finished sheet, preferred orientation will be prevalent unless the degree of cross rolling is carefully controlled. For most applications, a fair amount of directionality can be tolerated.

The property possessed by non-cubic metals of hardening rapidly under cold work is absent in zinc of commercial purities. There are four causes operating :

- (1) Heat of deformation raising the metal temperature above that of recrystallization.
- (2) As a general rule, recrystallization temperature falls as cold work increases.

(3) Effects of impurities on recrystallization temperature.

(4) Twinning, which may generate more planes favourably oriented for slip.

Annealing after cold rolling will usually result in grain growth, the sheet being already recrystallized. This may take place during storage at room temperature after rolling.

These causes explain in a general way the effects found by Chadwick in high-purity zinc, increase in strength and hardness due to limited cold rolling being lost owing to progressive recrystallization and grain growth during storage.

The steady increase in sclerescope hardness can be explained in the light of Mathewson and Phillips' ⁸ work on zinc single crystals by assuming that after severe cold rolling the preferred orientation of the crystals, originally 20°–25° towards the rolling direction, is such that the basal plane is parallel to the surface of the sheet. It is not known, however, whether such a preferred orientation has been confirmed.

The effects of annealing described by Ingall,¹² Burkhardt,⁶ and others do not fit in with present knowledge. While annealing above 150° C. would be expected to cause grain growth, and so a reduction of plasticity, an increase in hardness on annealing at temperatures below 150° C. is anomalous, unless it can be explained by the hardening effect of impurities on ageing.

It is clear that various aspects in the behaviour during rolling of zinc of the different commercial purities requires further examination, particularly in the light of recent research on the plastic deformation of metals.

IV.—ZINC-RICH ALLOYS.

Zinc-rich alloys for rolling can be divided roughly into two categories :

(1) Those in general use in all countries.

(2) Those used as war-time substitute materials or developed experimentally.

The majority of those in category 2 were developed in Germany before or during the recent war, mainly as substitutes for brass and other copper-base rolling alloys.

The compositions of the principal alloys are listed in Table II and the mechanical properties, where available, in Table III.

1. *Production of Rolling Slabs.*

Alloys in category 1 are cast, for the most part, in the same way as zinc; consequently there is little to add to what has already been said

on the subject. More elaborate methods are used in casting slabs of the alloys in category 2, the more important being described below.

Casting in Erichsen Moulds.

The base, which is water-cooled from below, is a copper plate over which there fits a rectangular frame to form the sides of the mould.

TABLE II.—*Compositions of Principal Zinc-Rich Rolling Alloys.*

Description of Alloy	Composition, %						
	Al	Cu	Pb	Mg	Mn	Cd	
Ductile Sheet (British)	0.3-0.4	Category 1
Engraving Sheet (British)	0.3-0.4	0.006-0.010	...	0.25-0.45	
Commercial Sheet (British)	0.8-1.3	
Zilloy 40 ¹⁷ (American)	...	0.85-1.25	0.1 max.	0.005 max.	
Zilloy 15 ¹⁷ (American)	...	0.85-1.25	0.15 max.	0.006-0.016	...	0.04 max.	
Zinc Foil Alloy . .	Zinc of 99.99% purity with 0.02-0.07 manganese added						
German Alloys : ¹							Category 2
Z410	4.0	1.0	...	0.04	
Z010	1.2	0.2	...	
Z020 { (a)	0.6	2.0	...	0.03	
(b)	2.0	...	0.03	0.6	...	
Z100	1.0	0.4	
Z1010	10.0	0.8	...	0.05	
Z1000	10.0	0.3	
Z040	0.2	4.0	
Z001 Mn	0.2	0.3	1.0	...	0.5	0.1	

TABLE III.—*Mechanical Properties of Principal Zinc-Rich Rolling Alloys in Cold-Rolled Condition.*

Description of Alloy	Ultimate Tensile Stress, tons/in. ²		Elongation, %		Brinell Hardness Number	Scleroscope Hardness Number
	Longitudinal	Transverse	Longitudinal	Transverse		
Ductile Sheet
Engraving Sheet
Commercial Sheet
Zilloy 40	13.5-17.5	20.0	5-10	3	...	20-28
Zilloy 15	16.0-21.0	24.0	5-10	2	...	20-30
Zinc Foil Alloy
German Alloys :						
Z410	22-25	26-30	2-5	2-4	80-100	...
Z010	14-16	16-19	30-60	20-50	40-60	...
Z020 { (a)	21-26	...	12-8	...	115-125	...
(b)	15-20	...	80-50	...	50-60	...
Z100	14-19	...	60-30	...	45-55	...
Z1010 *	27-29	...	12-8	...	90-100	...
Z1000 *	20-22	...	26-20	...	65-75	...
Z040 *	19-23	...	40-25	...	80-90	...
Z001Mn †	16-17	...	5	...	25-45	...

* Properties of the material in the extruded and drawn condition.

† Properties in the extruded condition.

This frame contains electrical heating elements and is insulated from the base by asbestos packing. Before casting, the heating elements are turned on to bring the surface of the sides to a temperature of 250°–280° C., at which point water cooling of the base is started. With slabs of dimensions 600 × 1100 × 100 mm., cast at a temperature 20°–30° C. above the melting point of the alloy, solidification is reported to take 20–25 min.

Casting in Vertical Moulds.

Details of design vary somewhat with this type of mould; they may be of the book variety or of solid sides with a hinged bottom for the ejection of the slab. Water-cooling systems may or may not be incorporated. Distributor funnels with three feeding tubes are generally used, the best practice being to mount the mould on a platform which can be lowered during the pouring operation so that the ends of the feeding tubes are maintained just below the metal surface.

Other Methods.

The vacuum-casting method is sometimes used, the procedure being similar to that described for zinc in Section II: 1. Semi-continuous casting methods appear seldom to be used for zinc-rich alloys.

2. Rolling.

Alloys in category 1 are fabricated by firms specializing in the rolling of zinc sheet, and the technique adopted is similar to that used for the latter material. Modifications are, of course, necessary. The alloys containing about 1.0% copper, for example, are rolled at a temperature around 220° C., while 190° C. is a suitable temperature for those containing appreciable quantities of cadmium. The cadmium-bearing alloys (which respond to work-hardening to some extent) receive the last finishing pass or two on rolls that are quite cold.

The majority of the alloys in category 2 were employed in Germany as substitutes for brass and were usually fabricated by firms which normally handled copper alloys. The mills used were designed originally for brass rolling and the methods of manufacture were based on brass-rolling practice.

The slabs are preheated for 4–16 hr. at temperatures varying with the composition of the alloy. Alloy Z410, for example, requires a temperature of 220°–260° C.

In hot rolling a larger number of light passes are necessary (as compared with brass), otherwise the excessive heat generated leads to cracking. Generally, after an initial reduction of 5% or so, a maximum

reduction of 20% per pass can be taken provided the rolls are water cooled. A certain amount of edge cracking appears to be unavoidable when rolling zinc alloy sheet or strip and edge trimming is necessary before cold rolling. The usual practice is to hot roll down to 6 or 8 mm., the subsequent cold rolling being done by pack or strip methods.

Intermediate annealing is necessary during the cold rolling of certain alloys. The alloy Z010, for example, requires a few hours at 180°–200° C. before final reduction by 20–40% to finished dimensions, this treatment improving the deep-drawing properties of the sheet. Certain other alloys are annealed at lower temperatures, and no annealing at all is required with alloy Z1010 which gets progressively softer with working.

Edge cracking occurs also in cold rolling, and the finished sheet or strip requires trimming. Before the last finishing pass the sheets are generally scrubbed with steel or fibre brushes or etched in a suitable reagent in order to obtain an improved surface.

3. Metallurgical Considerations.

Constitution of Alloys.

The alloys in category 1 are for the most part binary and their constitutions are fairly well established. Those in category 2 are based mainly on the zinc–aluminium–copper system with small additions of other elements in certain cases. The constitutions of the binary zinc–aluminium and zinc–copper alloys are well known, while recent work has clarified the zinc-rich corner of the ternary system to some extent.

The solubility of aluminium in zinc at room temperature is 0.08%, increasing to about 0.60% at 300° C., while the corresponding solubilities of copper in zinc are 0.20 and 1.5%, respectively. In ternary alloys the maximum solubility at the eutectic temperature (375° C.) is aluminium 1.3%, copper 2.9%. This decreases to 0.9% aluminium and 1.9% copper at 274° C. and is probably lower at lower temperatures. The influence of the presence of small quantities of cadmium, lead, magnesium, and manganese on the constitution of these alloys is for the most part unknown.

At the temperature of hot working it is probable that alloys Z100, Z010, and Z020a are single-phase or near single-phase, while the other alloys listed are almost certainly multi-phase at such temperature. All alloys are multi-phase at cold-working temperature.

Hot Rolling.

The alloys in category 2 are hot rolled at temperatures considerably above those used for pure and commercial zinc and the temperature

range over which hot work can be carried out is often limited. Alloy Z410, for example, shows a maximum elongation at 200° C. and a maximum reduction of area at 260° C.,⁶ indicating a working range between 200° and 300° C.; while an alloy of composition copper 4, bismuth 0.3, manganese 0.3, aluminium 0.3% possesses high plasticity only between 320° and 360° C., the elongation and reduction-of-area figures falling sharply above and below this range.⁶

The heat generated in zinc by deformation is considerable and temperature during hot rolling obviously requires careful control.

Cold Rolling.

The effect of cold work on the mechanical properties of the zinc-rich alloys varies with composition, and the data available are insufficient to permit any generalization.

An alloy of composition copper 4, aluminium 0.2% is reported⁶ to lose ductility with cold reduction up to 30%, but further reduction to 60% results in an increase to a figure higher than that of the original material. The reverse effect is found when 0.1% lithium is added to this alloy, ductility reaching a maximum at 30% cold reduction and thereafter declining. An alloy containing 4% aluminium responds to cold work in a similar way, ductility decreasing after an initial increase.

It appears, however, that in no case is the decrease in ductility of zinc-rich alloys during cold reduction comparable in magnitude with that which occurs when most other metals are so worked.

Effect of Impurities.

The effect of impurities on the mechanical and rolling properties of the alloys in category 2 varies somewhat with alloy composition.

As with unalloyed zinc, tin causes hot shortness in these materials and is kept below 0.002%, except in those alloys containing substantial percentages of aluminium, when up to 0.011% is tolerable from the point of view of hot rolling.

The presence of less than 0.7% lead in aluminium-free alloys appears to have little effect on rolling or mechanical properties. When cadmium in excess of 0.04% is also present, such alloys become hot short, while at lower temperatures strength increases at the expense of ductility. Lead, cadmium, and tin increase greatly the susceptibility to intercrystalline corrosion of zinc-aluminium alloys, and for this reason can be tolerated in such alloys only in very small percentages.

Iron up to 0.2% has little effect on the rolling properties of zinc-copper alloys, but ductility is adversely affected even by smaller

quantities.¹⁸ The harmful effect of this impurity appears to be more marked in those alloys containing aluminium and magnesium together, and in such alloys 0.005% is the maximum amount of iron permissible.

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THE BEHAVIOUR OF NICKEL-CHROMIUM-IRON ALLOYS IN CARBON-BEARING GASES IN THE RANGE 900°-1000° C.*

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SYNOPSIS.

An investigation is reported into the cause of corrosion of nickel-chromium electrical-resistor alloys used at temperatures of 900°-1000° C. in an atmosphere of partially burnt town's gas. The corrosion, which is shown to be due to simultaneous carburization and oxidation of the alloy, with rapid intergranular oxidation in depth, is typical of that known as "green rot". The order of attack is less in alloys containing iron, and the presence of approximately 2% silicon in an alloy is sufficient to suppress the corrosion completely.

The possible factors governing the corrosion mechanism are discussed, and the importance of the oxide layer as a barrier to carbon entry into the matrix is demonstrated.

I.—INTRODUCTION.

THE use of nickel-chromium alloys for high-temperature service is well established. The main requirement which these materials have had to meet has been that of possessing a minimum scaling rate compatible with reasonable strength either in air or in flue gases, and it has been on this basis that the relative merits of particular alloys have been assessed. In more recent years, however, these alloys have been used to an increasing extent under conditions other than those where free oxygen is present, as, for example, for furnace components exposed to bright-annealing and carburizing atmospheres, and for gas-turbine parts. It does not necessarily follow that the most suitable alloy for use under such conditions is the one which will give satisfactory performance in air, and it is important that the behaviour of a material recommended for high-temperature service should be assessed with reference to the particular atmosphere in which it is to be used.

Electric furnaces for the heat-treatment of metals are used in many cases in conjunction with a controlled atmosphere. In certain types

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of furnaces, both the electrical resistors and the charge are exposed to the same gases; in others, the work is enclosed by a cover of suitable heat-resisting material and the resistors are exposed to air. The use of controlled atmospheres free from carbon-bearing gases does not introduce any metallurgical problems associated with the performance of the materials used for covers and resistors; the life of such components is also satisfactory when the material is exposed to certain types of atmospheres generated by the partial burning of a fuel gas (such as burnt town's gas of the following composition :

CO₂ 5%; CO 10%; H₂ 15%; H₂O 2.3%; N₂ remainder).

Nevertheless it has been found that under certain conditions nickel-chromium alloys may corrode very rapidly in burnt fuel gases, and develop a type of corrosion which has been termed "green rot".

Figs. 1 and 2 (Plate LXXVIII) show electrical resistors which have developed "green rot". The resistors were made of best-quality commercial 80:20 nickel-chromium alloy strip, approximately $\frac{1}{8}$ in. thick, and had been in service for about six months in a furnace operating at 950° C., during which time they had been continuously exposed to desulphurized burnt town's gas of the following nominal composition :

CO₂ 7%; CO 14%; H₂ 14%; H₂O 2.3%; N₂ remainder.

The corroded material showed severe embrittlement, but no "hot spots" had developed even on the most severely attacked section, indicating that the conductivity of the alloy had not deteriorated appreciably. In certain parts the element surface was blistered, and the corrosion extended almost completely through the section of the strip.

X-ray examination of the corrosion products indicated that the main constituent was chromic oxide, associated with a small concentration of nickel oxide. X-ray and chemical tests for sulphur were negative. Samples were machined from the corroded section, and the various machined cuts were analysed chemically for chromium and carbon, with the results shown in Table I.

TABLE I.—*Composition of Corroded Elements at Various Depths below the Surface.*

No. of Cut	Range, in.	Cr, %	C, %
1	0.00/0.010	18.3	0.05
2	0.010/0.020	19.4	0.08
3	0.020/0.030	20.3	0.11
4	0.030/0.040	20.6	0.13

In addition, part of the corroded specimen was subjected to anodic attack in 20% hydrochloric acid solution, and the residues from the outer and underlying layers were collected and examined by X-rays. The residue from the outer layer was shown to contain mainly chromic oxide, and that from the underlying layer mainly the chromium carbide, Cr_7C_3 . Figs. 3–6 (Plates LXXVIII and LXXIX) show sections through the corroded areas, together with one through a relatively non-corroded portion of the element, which may be considered as being in a condition comparable to that of the resistor before use. It will be noted that below the outer oxidized layer there is a region of fairly heavy carbide precipitation, confined mainly to the grain boundaries. At the extreme inner edge of the oxidized zone, oxides are seen to be forming in those sites occupied by the chromium carbide particles.

Examination of the internal structure of the furnace in which the resistors had been in service showed that a considerable deposition of carbon had occurred in and near to the gas inlet ports to the heating chamber, suggesting that the atmosphere used in the furnace had been richer in carburizing constituents than burnt town's gas of the nominal composition quoted above. It was later confirmed that for lengthy periods the concentration of methane in the burnt town's gas supplied to the furnace had been permitted to rise very considerably above 1%. After precautions had been taken to ensure that the specified atmosphere composition was maintained, no further rapid corrosion of this type was reported.

This preliminary survey of the problem indicated that the corrosion was associated with the presence of carbides in the alloy. As there is an increasing industrial interest in the gaseous process for carburization and the heat-treatment of high-carbon-bearing alloys, it is important that materials should be available for furnace construction which are not susceptible to rapid corrosion of the type indicated above. The present paper describes an investigation of the corrosion-resistance of certain nickel-chromium alloys in carbon-bearing gases within the temperature range 900°–1000° C.

II.—PREVIOUS WORK.

There are numerous published papers in which the reduction of the corrosion-resistance of alloys is attributed to the formation of alloy carbides. The susceptibility of nickel-chromium-iron alloys to intergranular carbide precipitation is well known. Bain, Aborn, and Rutherford¹ associate the resulting decrease in corrosion-resistance with the loss of chromium from solid solution at the grain boundaries,

while Newell² has pointed out that the corrosion behaviour of 18 : 8 stainless steels after heating is controlled by the carbon content and by the "grain boundary extent" (i.e. grain-size) available for carbide precipitation.

Many workers have drawn attention to the increased rate of corrosion of nickel-chromium-iron alloys in carbon-bearing gases. The particular failures encountered have included heating elements,^{3,4} cracking-still tubes operating at 650° C.,⁵ and aircraft exhaust manifolds.^{6,7} While in all these cases carburization of the alloy has been observed, no indication of the mechanism of corrosion has been suggested. Other workers⁸⁻¹¹ have reported the beneficial effect of iron, and particularly of silicon, in nickel-chromium-base alloys in resisting corrosion under carburizing conditions at temperatures near to 1000° C. Recently Bucknall and Price¹² have investigated the corrosion of nickel-chromium electrical resistors in a variety of atmospheres and have demonstrated that corrosion can occur in the presence of carburizing gases. Rapid corrosion was developed only in atmospheres of the partially burnt town's gas type to which active carburizing agents had been added. The addition of silicon to the nickel-chromium alloy reduced considerably the rate of attack, and it was suggested that its effect lay in its ability to scavenge oxygen from a chromium-free surface layer. The addition of iron was also found to be beneficial; its function was considered to be similar to that of silicon, since the iron would be more readily oxidized than nickel, and thus the maximum oxygen pressure in the matrix would be maintained at a lower level than would be the case in the absence of iron. Hickman and Gulbransen¹³ have shown that minor quantities of silicon improve the oxidation resistance of 80 : 20 nickel-chromium alloys, and have suggested that silicon retards the diffusion of nickel to the surface.

III.—EXPERIMENTAL INVESTIGATION.

The alloys selected for the laboratory investigation were supplied by The Mond Nickel Co., Ltd., in the form of $\frac{3}{8}$ -in.-dia. hot-rolled rod. Details of the composition of the alloys Nos. I-V are given in Table II, from which it will be noted that they fall into two broad categories : Nos. I, II, and V were nickel-chromium-iron alloys, No. V containing in addition approximately 2.5% silicon; Nos. III and IV were nickel-chromium alloys, the latter containing in addition approximately 3.37% iron and 2.5% titanium. Spectrographic analysis showed traces of copper in all alloys, and vanadium in alloys I and IV.

The general experimental procedure was to expose prepared test-

pieces of the various alloys to a controlled atmosphere within the temperature range 900°–1000° C. and to follow the course of corrosion by noting any change of weight and by metallographic examination. The test specimen, 3 in. long, was lightly polished with emery paper to remove any visible surface scale, degreased in acetone, dried, and weighed. The weighed specimen, in a supporting quartz boat, together with a similar unweighed specimen of identical composition, was charged into a quartz tube, which in turn was heated by a tubular electric-resistance furnace. A stream of a controlled atmosphere was maintained through the furnace tube throughout the period of test, which, in almost every case, extended to 500 hr. At intervals, the specimens were removed from the furnace tube and a slice cut from the unweighed sample for metallographic examination, while the specimen in the quartz boat was weighed. Both samples were then returned to the furnace tube and the test continued.

TABLE II.—*Composition of Alloys Used in the Investigation.*

Alloy No.	Chemical Analysis *								
	Ni, %	Cr, %	Fe, %	Mn, %	Co, %	Ti, %	Al, %	Si, %	C, %
I	78.88	13.78	6.21	0.31	...	0.26	0.13 †	0.49	0.04
II	64.90	14.62	19.37	0.97	0.24	0.07
III	76.41	21.12	0.86	0.35	...	0.34	0.09	0.72	0.10
IV	72.08	20.36	3.37	0.38	...	2.54	0.31 †	0.82	0.09
V	37.63	17.73	40.75	1.27	2.38	0.12
KHC	78.72	19.71	0.29	0.38	0.23	0.54	0.05
KHG	64.77	14.70	19.14	1.19	0.23	0.09
KHI	62.96	20.67	14.12	0.12	2.21	0.06

* Spectrographic analysis showed also traces of copper in alloys I–V and vanadium in alloys I and IV.

† X-ray examination of the aluminium precipitates for these determinations showed that the precipitates were slightly contaminated, the estimated purity of the precipitates being 80–90% (I) and 95% (IV). No correction has been applied for the impurity.

Two types of controlled atmospheres were used in the experimental work. One was typical of that in commercial use for the bright annealing of mild steel and had the following average composition :

CO₂ 4.5%; CO 13%; CH₄ 1%; H₂ 14%; H₂O 2.3%; N₂ remainder.

The other atmosphere was more representative of that used for industrial gas-carburizing processes, and was prepared by removing the carbon dioxide and water vapour from the previous atmosphere, by absorption in caustic soda and activated alumina respectively, and adding to the resulting mixture 2% of propane.

TABLE III.—*Nature and Depth of the Phase Separation Occurring at the Surface of Resistor-Element Materials after Treatment in the "Carburizing" Atmosphere.*

The depth below the surface to which each section of corroded area extends is indicated (in 1/1000 in.) under the appropriate headings in the Table.

Specimen	Alloy I—80 : 13 : 7 Ni-Cr-Fe				Alloy II—65 : 15 : 20 Ni-Cr-Fe				Alloy III—80 : 20 Ni-Cr (Standard)				Alloy IV—80 : 20 Ni-Cr (+2½% Ti)				Alloy V—37 : 18 : 2 Ni-Cr-Si			
	Temp., ° C.	Time, Hr.	Oxide	White Band	Region X	Region Y	Oxide	White Band	Region X	Region Y	Oxide	White Band	Region X	Region Y	Oxide	White Band	Ppt.	Oxide	White Band	Ppt.
900	5		2	25	Scale	...	4	20	...	1	10	10	Very light to centre
	75		Fil 7	1	60	70	Fil 2	1	25	80	...	2	Not deter-	25	Fil 1	2
	150		Fil 6	...	75	150	Fil 4	1	75	120	Fil 1	1½-3½	18-40	60	Fil 2	4
	300		Fil 6	...	100	120	Scale	1	75	100	Scale	3	60	90	Fil 2	5
	500		Scale	2	75	150	Scale	2	85	To centre	Fil 4	4	80	150	Scale	6
				A Ppt.				A Ppt.				A & B Ppt.				Mainly B Ppt.; some A Ppt.				
950	5		...	1	10	30	...	1	10	100	...	1	5	10	Light to centre
	75		Fil 1	2	30	70	Fil 3	1	60	150	...	3½	approx.	25	...	1½
	150		Fil	2-3	40	80	Fil 5	1½	60	150	Fil	2-3	40	40	Fil 1	6
	200		Fil	3	70	150	Scale	2	75	180	...	3	50	50	Fil 1	4-6
	500		Fil	4	100	150	Scale	1½	100	To centre	...	4½	60	70	Scale	7
				A Ppt.				A Ppt.				A & B Ppt.				Mainly B Ppt.; some A Ppt.				
1000	5		...	1	12	...	Fil	1	25	50	...	1	8	10	Faint throughout
	75		Scale	2	40	...	"	2	50	To centre	...	2	50	25	Fil 2	4
	200		...	3	50	...	"	4	120	To centre	...	2	60	45	Fil 2	5
	400		...	3	140	Thro'- out	"	4	150	To centre	...	6	100	25- 50	...	10
	500		...	6	150	"	"	4	To centre	...	Fil	6	120	...	Not deter- min- able
				A Ppt.				A Ppt.				A & B Ppt.				Mainly B Ppt.; some A Ppt.				

For notes to Table III, see p. 587.

IV.—DISCUSSION OF RESULTS.

It was not found possible to obtain any reliable or consistent indication of the rate of attack of any of the alloys in either of the two atmospheres used, by following the changes in weight of the specimens after exposure. This partly resulted from the complicating effect of carbon deposition around the specimens, which was particularly severe after treatment in the carburizing atmosphere. Furthermore, as will be shown later, the mechanism of the corrosion itself is such as to make it most difficult to follow its progress in this way.

Figs. 7–14 (Plates LXXX and LXXXI) show microsections of materials Nos. II, III, IV, and V after treatment at 950° C. for 5 hr. and 500 hr., respectively, in the carburizing atmosphere (material No. I was in all respects very similar to material No. II). It may be seen that the attack on materials Nos. II and III was much heavier than, and in some respects different from, that on alloys Nos. IV and V. At the surface of all the alloys an oxide coating may be observed and beneath it a band into which oxide penetration may occur, but which is superficially free from precipitated carbides—a “white band”. Beneath this band there is an extensive zone in which precipitates of two types are visible: (a) rods and threads which occur both within and around the grains (as in Fig. 20, Plate LXXXIII); and (b) dispersed spheroids only, slightly more concentrated at the grain boundaries than within the grains.

Figs. 7–14 illustrate the difference in the types and amount of precipitation; the structure of material No. II exhibits mainly type (a) and No. V exhibits type (b) only. Alloys III and IV fill intermediate positions, although alloy No. III does not differ greatly from alloy No. II. The attack is obviously much greater in the case of type (a), in which intergranular oxide penetration is very marked, whereas such penetration is not observed in the case of type (b). In Table III are summarized the types of structure observed in specimens which were examined after treatment at the temperatures indicated.

NOTES TO TABLE III.

The compositions quoted are nominal; for analyses see Table II.

Region X—From oxide layer down to the approximate line where carbide precipitation within the grains is no longer visible.

Region Y—From oxide layer down to the approximate line where carbide precipitation around the grains is no longer visible.

TYPES OF PRECIPITATION.

A.—Grain-boundary filaments, laths on cleavage planes, and small discrete globules away from either.

B.—Fairly well dispersed globules, only faintly concentrated on grain boundaries.

KEY.

Scale = Continuous oxide.

Fil = Filament of intergranular oxide.

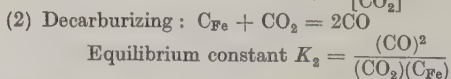
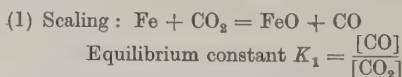
Microsections of the materials taken after treatment in the bright-annealing atmosphere gave no evidence of the rapid corrosion which had occurred in the carburizing atmosphere. Some similar characteristics were present, i.e. an oxide layer and a "white band", but the precipitation of carbide was not extensive in any of the specimens. Figs. 15-18 (Plate LXXXII) show the edges of the materials after treatment for 500 hr. at 1000° C. in partially burnt town's gas. Dispersed carbide particles are visible in all the photographs, but there is no indication in any of them that these particles have resulted in the formation of oxide; no one alloy seems superior to the others in its behaviour under these conditions of test.

V.—MECHANISM OF CORROSION.

The analysis of the original corroded element, the identification of carbides below the oxidized zone, and the susceptibility of standard nickel-chromium material to carbide precipitation, as indicated by the experimental work, all suggest that the primary cause of rapid attack is carburization of the base material, leading to precipitation of chromium carbide. This precipitation denudes the matrix of chromium, and the rate of progression of the oxide increases, especially in the case where carbide is formed at the grain boundaries. Figs. 19 and 20 (Plate LXXXIII) show a matrix containing typical grain-boundary precipitation of carbide in which the oxide can be seen enveloping the carbide particles. Thus, although carburization and oxidation are occurring simultaneously, the rate of progress of the oxide layer, at any instant, is controlled by the distribution of the carbide particles which have been formed at an earlier stage of carburization. The factors which may govern this process are discussed below.

(a) *Atmosphere.*

When a plain carbon steel is heat-treated, the atmosphere surrounding it usually has to be such as to prevent either scaling or both scaling and decarburization. In an atmosphere containing carbon monoxide and carbon dioxide the pertinent reactions are the following :



At a given temperature there are definite values of the ratios $(\text{CO})/(\text{CO}_2)$ and $(\text{CO})^2/(\text{CO}_2)$ which must be maintained in order to prevent scaling



FIG. 1.—Surface of Corroded 80:20 Nickel-Chromium Resistor. $\times 2$.



FIG. 2.—Section through Corroded 80:20 Nickel-Chromium Resistor. $\times 5$.

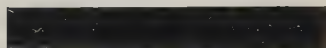


FIG. 3.—80:20 Nickel-Chromium Resistor, as supplied. $\times 50$.

[To face p. 588.]



FIG. 4.—Uncorroded Section of 80:20 Nickel-Chromium Resistor, ex furnace. $\times 200$.

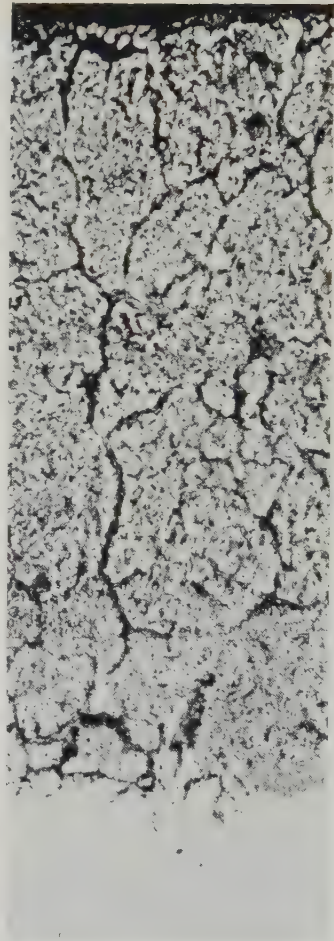


FIG. 5.—Corroded Section of 80:20 Nickel-Chromium Resistor, ex furnace. $\times 50$.

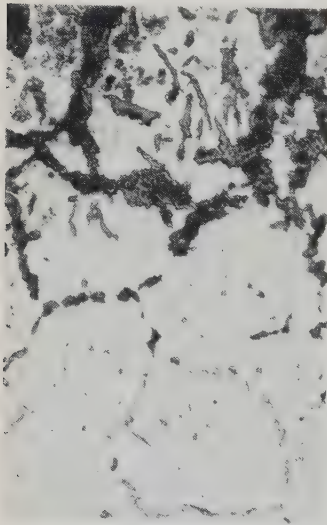
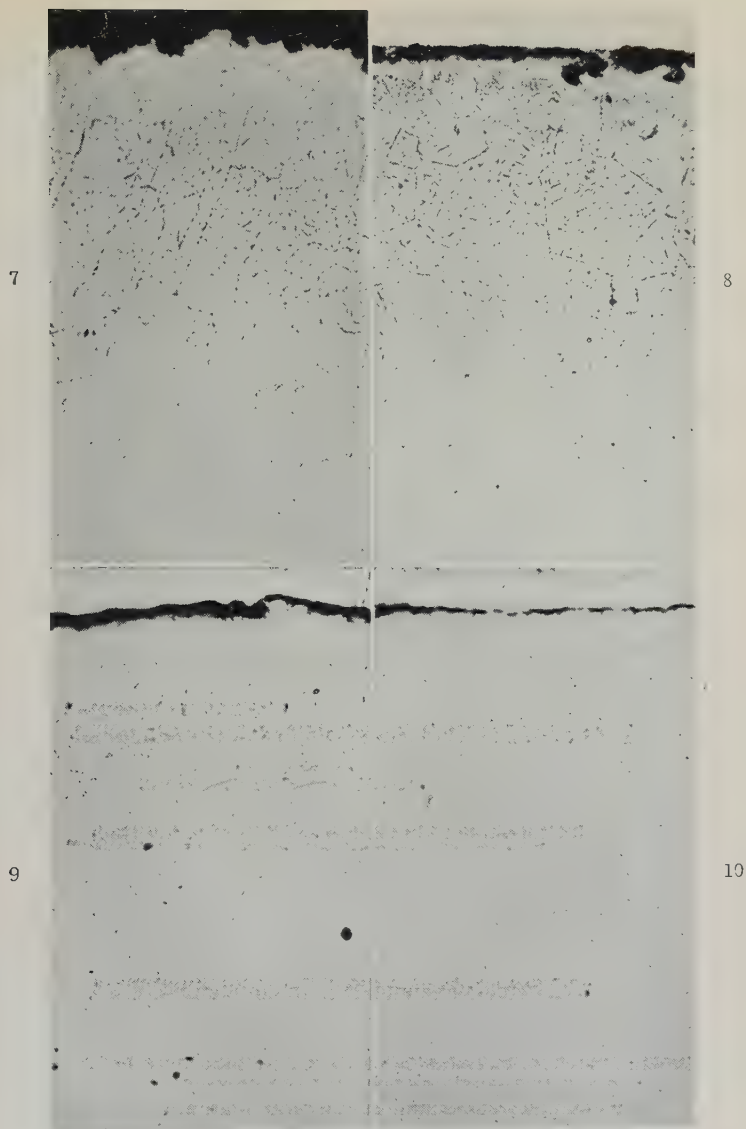


FIG. 6.—As Fig. 5, Showing Progression of Oxide Layer. $\times 200$.



FIGS. 7-10.—Alloys treated at 950°C. , in burnt town's gas (free from CO_2 and H_2O) + 2% propane, for 5 hr. $\times 200$.

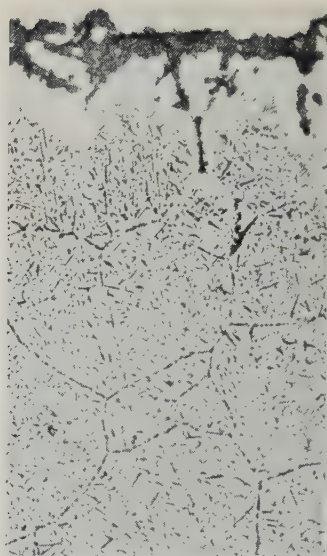
FIG. 7.—Alloy No. II.

FIG. 8.—Alloy No. III.

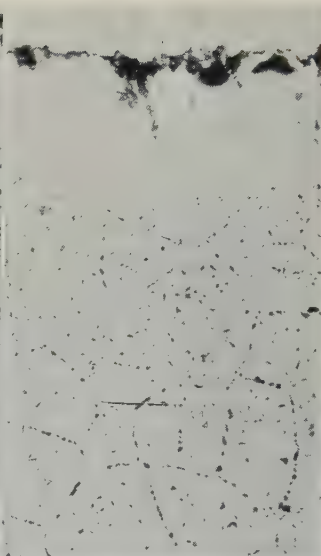
FIG. 9.—Alloy No. IV.

FIG. 10.—Alloy No. V.

11



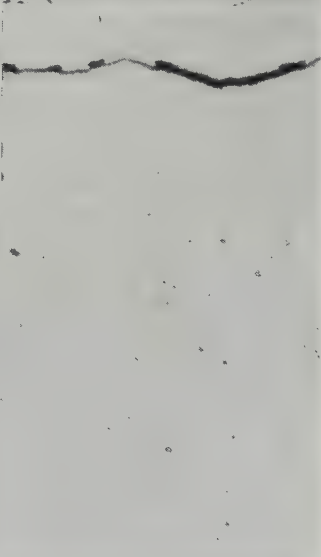
12



13



14



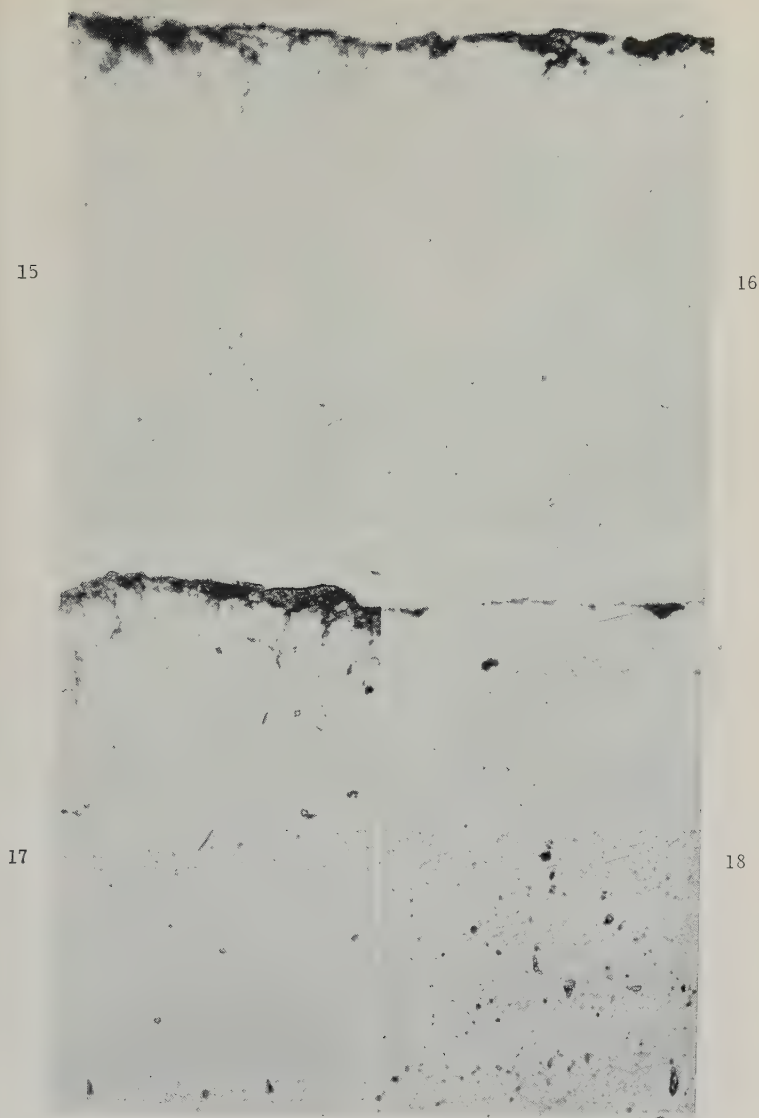
FIGS. 11-14.—Alloys treated at 950° C., in burnt town's gas (free from CO_2 and H_2O) + 2% propane, for 500 hr. $\times 200$.

FIG. 11.—Alloy No. II.

FIG. 12.—Alloy No. III.

FIG. 13.—Alloy No. IV.

FIG. 14.—Alloy No. V.



FIGS. 15-18.—Alloys treated at 1000° C. in burnt town's gas for 500 hr.
× 200.

FIG. 15.—Alloy No. II.

FIG. 17.—Alloy No. IV.

FIG. 16.—Alloy No. III.

FIG. 18.—Alloy No. V.

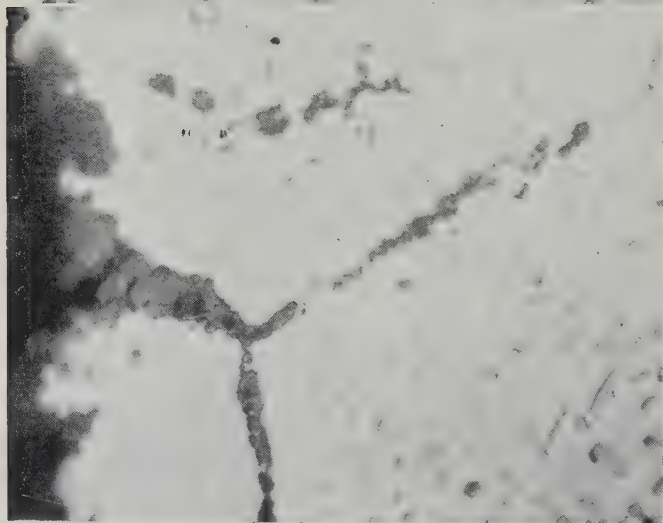
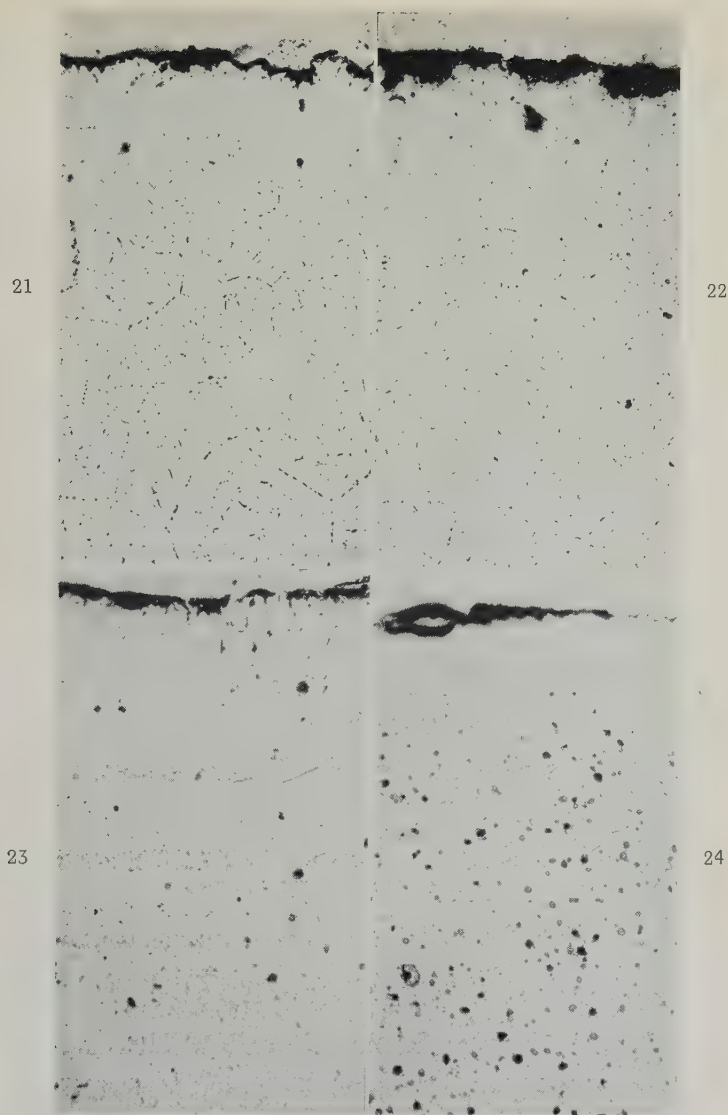


FIG. 19.—Alloy No. II treated at 900° C., in burnt town's gas (free from CO_2 and H_2O) + 2% propane, for 500 hr., showing oxidation at edge.
× 1000.



FIG. 20.—Alloy No. II treated at 950° C., in burnt town's gas (free from CO_2 and H_2O) + 2% propane, for 500 hr., showing oxidation of carbides.
× 1000.



FIGS. 21-24.—Alloys treated at 950° C., in burnt town's gas (free from CO_2 and H_2O) + 2% propane, for 500 hr. and quenched. $\times 200$.

FIG. 21.—Alloy No. II (cf. Fig. 11).
FIG. 23.—Alloy No. IV (cf. Fig. 13).

FIG. 22.—Alloy No. III (cf. Fig. 12).
FIG. 24.—Alloy No. V (cf. Fig. 14).

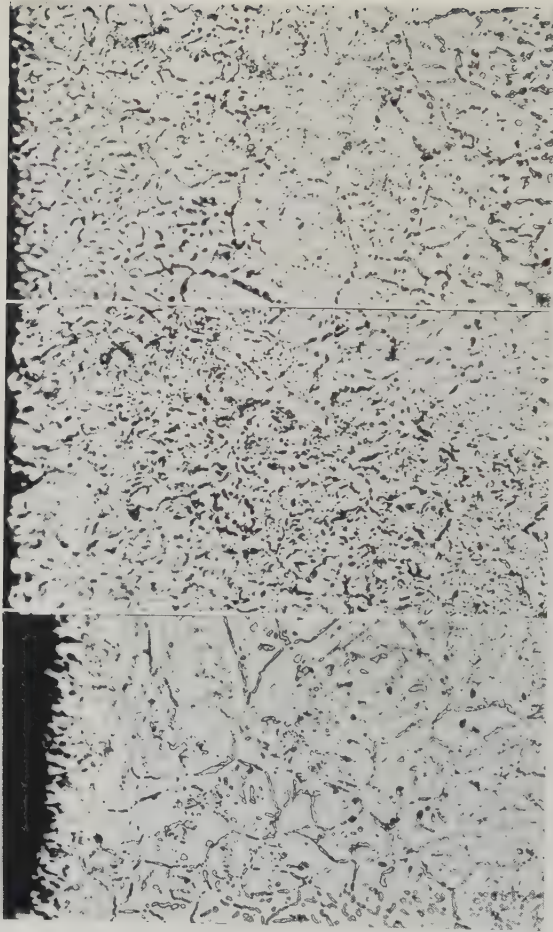


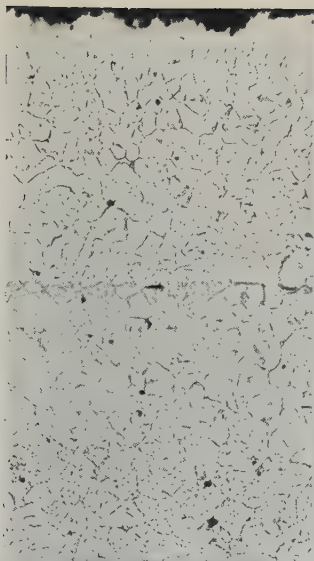
FIG. 25.—Alloy KHC.

FIG. 26.—Alloy KHG.

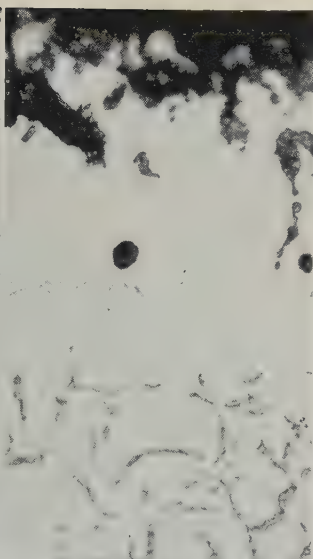
FIG. 27.—Alloy KHL.

FIGS. 25-27.—Alloys carburized for 75 hr. at 1000° C. in dry hydrogen + 3% propane. $\times 200$.

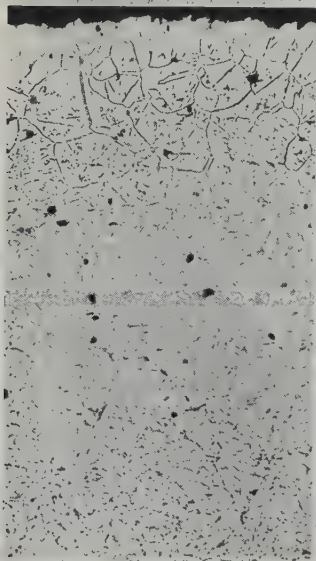
28



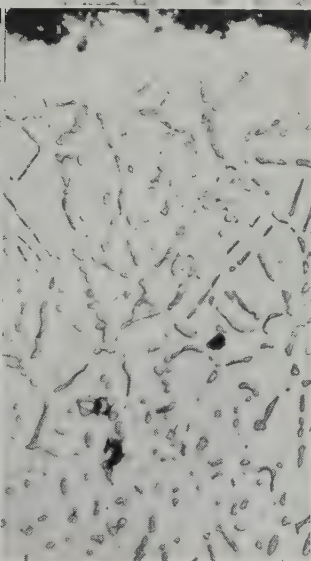
29



30



31



FIGS. 28-31.—Alloys treated first as in Figs. 25-27, then for 80 hr. at 1000° C. in wet hydrogen (2.5% H_2O).

FIG. 28.—Alloy KHC. $\times 100$.
FIG. 30.—Alloy KHG. $\times 100$.

FIG. 29.—Alloy KHC. $\times 500$.
FIG. 31.—Alloy KHG. $\times 500$.

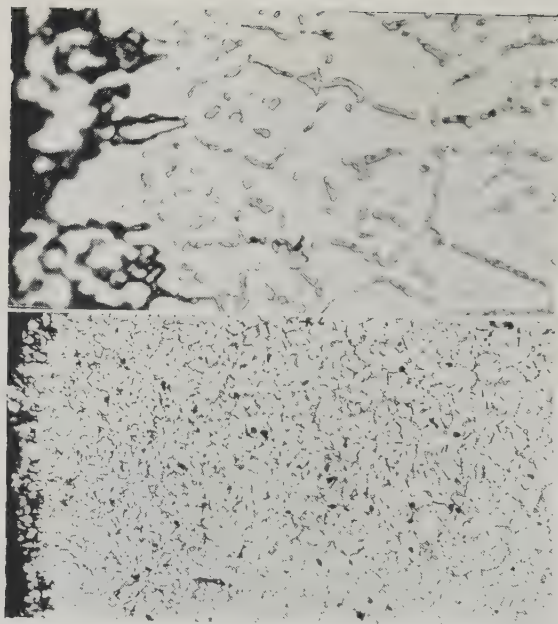


FIG. 32. Alloy KHI carburized for 75 hr. at 1000° C. in dry hydrogen + 3% propane, then treated for 80 hr. at 1000° C. in wet hydrogen (2.5% H₂O).
× 100.

FIG. 33.- Alloy KHI treated as in Fig. 32. × 500.

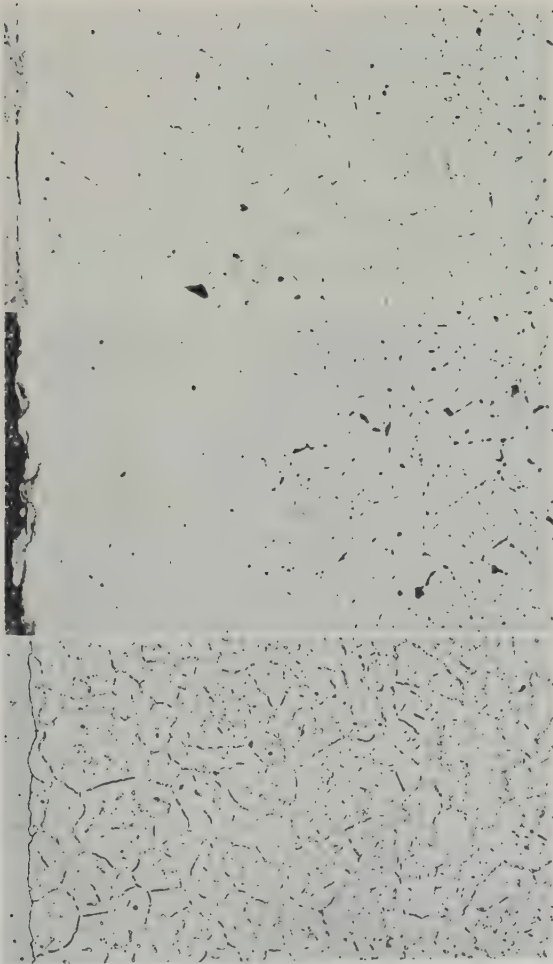


FIG. 34.—Alloy KHC carburized for 75 hr. at 1000° C. in dry hydrogen + 5% propane. $\times 200$.

FIG. 35.—Alloy KHC treated as in Fig. 34, then decarburized for 15 hr. at 1000° C. in dry hydrogen. $\times 200$.

FIG. 36.—Alloy KHC treated as in Fig. 35, then decarburized for 25 hr. at 1000° C. in wet hydrogen (2.5% H_2O). $\times 200$.

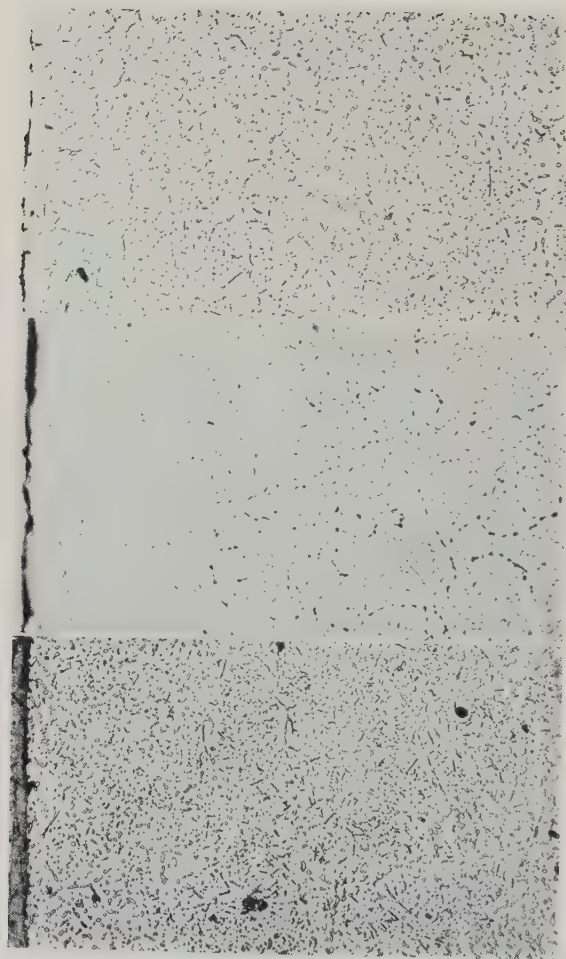


FIG. 37.—Alloy KHG carburized for 75 hr. at 1000° C. in dry hydrogen + 3% propane. $\times 200$.

FIG. 38.—Alloy KHG treated as in Fig. 37, then decarburized for 15 hr. at 1000° C. in dry hydrogen. $\times 200$.

FIG. 39.—Alloy KHG treated as in Fig. 38, then decarburized for 25 hr. at 1000° C. in wet hydrogen (2.5% H_2O). $\times 200$.

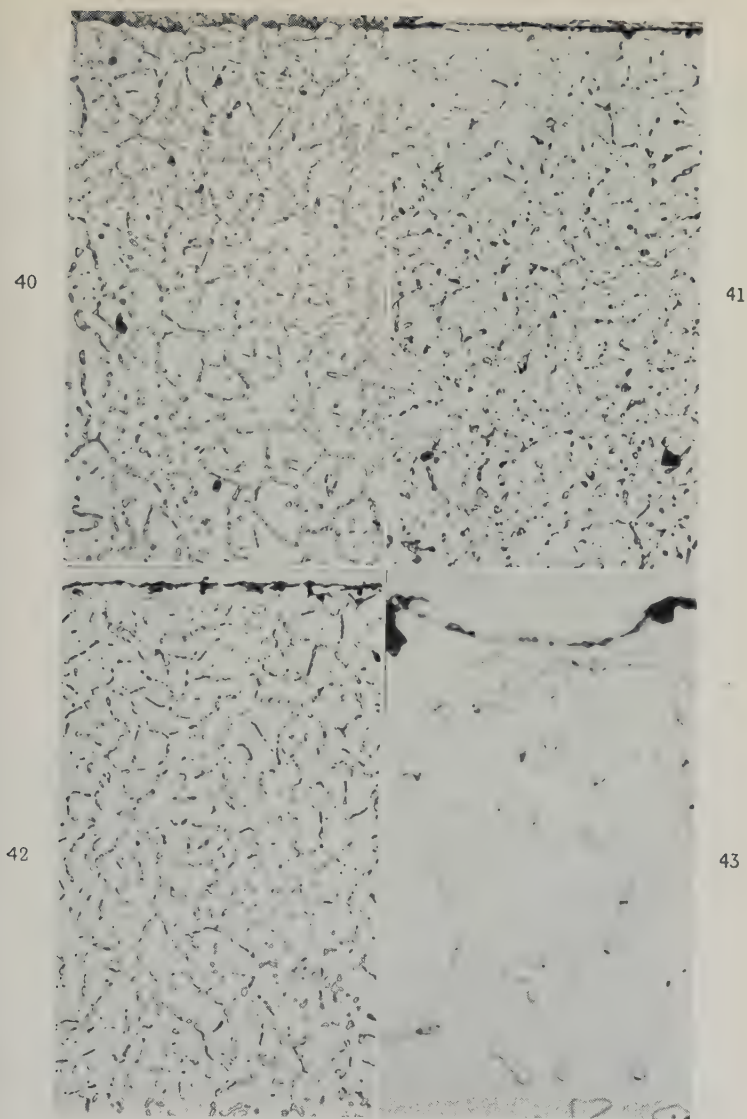


FIG. 40.—Alloy KHI carburized for 75 hr. at 1000° C. in dry hydrogen + 3% propane. $\times 200$.

FIG. 41.—Alloy KHI treated as in Fig. 40, then decarburized for 15 hr. at 1000° C. in dry hydrogen. $\times 200$.

FIG. 42.—Alloy KHI treated as in Fig. 41, then decarburized for 25 hr. at 1000° C. in wet hydrogen (2.5% H_2O). $\times 200$.

FIG. 43.—Alloy KHI treated as in Fig. 42. $\times 1000$.

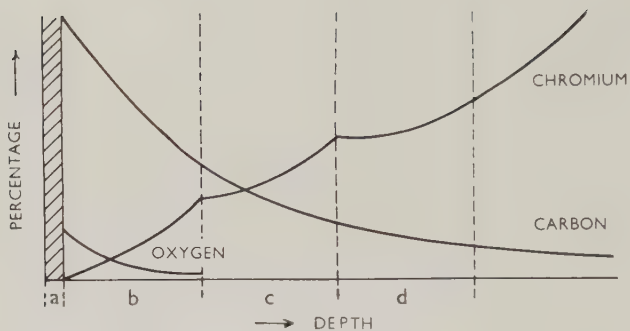


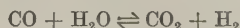
FIG. 44 — Supposed Variation of Concentration of Oxygen, Chromium, and Carbon in Solution Near Edge of Specimen.

Region	Phase
<i>a</i>	Oxide
<i>b</i>	No precipitate
<i>c</i>	$\text{Cr}_a\text{C}_\beta$
<i>d</i>	$\text{Cr}_\gamma\text{C}_\delta$

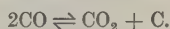
$$(a/\beta > \gamma/\delta)$$

or decarburization taking place. It will be apparent that although there may be sufficient carbon dioxide relative to carbon monoxide in the atmosphere to cause oxidation of the metal, nevertheless, at the same time these gases would be in equilibrium with a definite amount of carbon in the steel; on unalloyed steels this effect is normally masked by the occurrence of scaling, which may be comparatively rapid. In a heat-resisting steel, which forms a protective oxide coating, the rate of scaling is low, and thus the tendency of the surrounding atmosphere to raise or lower the total carbon concentration in the metal becomes more important. Any alloy containing chromium will be able to contain, at a fixed temperature, some definite maximum carbon concentration in solution, and corresponding to this maximum concentration there will be a definite value of the ratio $(\text{CO})^2/(\text{CO}_2)$ in the surrounding atmosphere. An atmosphere containing carbon monoxide and carbon dioxide in quantities such that the ratio $(\text{CO})^2/(\text{CO}_2)$ is greater than this equilibrium value, may cause corrosion of the carburization-oxidation type, since it is capable of producing within the metal precipitated chromium carbide which may later become converted to chromium oxide.

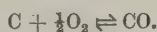
The concentrations of carbon monoxide and carbon dioxide taken to evaluate the expressions $(\text{CO})/(\text{CO}_2)$ and $(\text{CO})^2/(\text{CO}_2)$ are not necessarily those which obtain in the original gas mixture, since inter-gas reactions, such as :



will tend to promote a general state of equilibrium in the gas phase at the temperature of treatment. The values which should be used, therefore, are those existing after this state of equilibrium has been assessed. Furthermore, as the concentration of carbon monoxide in a gas mixture is increased relative to that of carbon dioxide, a point is eventually reached where free carbon will be produced by the reaction :



It is probable that at and after this point the carburization potential is static, as free carbon is present and the oxidation potential then *increases* with increasing carbon monoxide concentration, since the oxidation potential is governed by the reaction :



Thus, by continually increasing the carbon monoxide content of a gas mixture, a maximum carburization potential is achieved and maintained, whereas a minimum oxidation potential is attained at only one value of carbon monoxide concentration.

The effect of the relative carburizing potential of the two atmospheres used in the experiments is shown by the greater degree of carbide precipitation in those materials treated in the atmosphere free from decarburants, and containing propane. Precipitation of carbides in the standard burnt town's gas is only slight.

(b) *Superficial Oxide Layer.*

The life of a nickel-chromium element in air depends upon the nature of the oxide coating which is formed. Metals of the oxidation-resistant type have a rate of scaling given by $x^2 = kT$, where x is the rate of metal scaled in time T , and :

$$k = Ae^{-\frac{Q}{RT}}$$

The scaling rate is dependent upon the free energy of formation of the oxide, the relative mobilities of positive and negative ions through the scale, and the conductivity of the oxide. In the particular type of corrosion occurring in carburizing atmospheres, it is of importance to know what resistance, if any, the oxide formed offers to carbon penetration.

In order to investigate any differences which might occur in the nature of the oxide layers formed on these alloys, the metals were treated in air for 500 hr. at 950° C. and the resulting oxide was subjected to X-ray analysis. Although the oxide coatings were not identical, all

TABLE IV.—*Nature of Oxides on Surface after Oxidation in Air at 950° C. for 500 Hr.*

Alloy No.	X-Ray Analysis	
	Phases Detected	Remarks
III	NiO.Cr ₂ O ₃ —strong NiO—medium Cr ₂ O ₃ —weak	NiO.Cr ₂ O ₃ has the spinel-type structure and a lattice constant $a_0 = 8.31$ kX. units.
IV	Cr ₂ O ₃ ; NiO.Cr ₂ O ₃ —strong NiO—weak Unidentified phase—very weak	The concentrations of the two phases Cr ₂ O ₃ and NiO.Cr ₂ O ₃ are approx. equal.
V	A spinel-type phase—strong Cr ₂ O ₃ —medium NiO—very weak	The lattice constant of the phase having the spinel-type structure is rather larger than that corresponding to the formula NiO.Cr ₂ O ₃ . It is probable that the Fe present in the alloy has partially replaced the Cr, thus enlarging the unit cell.

the samples possessed the spinel type of coating, NiOCr_2O_3 , which is characteristic of these heat-resisting alloys. X-ray analysis of the coatings gave no indication of any major difference to which the varying behaviour of the materials might be attributed (Table IV). Hence the effect of the titanium and silicon in the more resistant alloys (Nos. IV and V) on the nature of the oxide could not be assessed by this means. The X-ray examination was conducted on the bulk of the scale, but it is well known that minor elements may influence markedly the nature of the oxide film at the metal/metal-oxide interface and, since the barrier to carbon entry into the matrix may be at this interface only, it cannot be assumed that the oxide layer is not a factor in controlling this type of corrosion.

(c) *Base Alloy.*

If the restriction of carbon precipitation in the base alloy is necessary to prevent corrosion, then the maximum amount of carbon that may be retained in solution at the operating temperature is critical. Obviously, the alloy which has a higher carbon solubility than another may be maintained in an atmosphere of high carburizing potential without the danger of this form of corrosion occurring.

If the first carbide to be formed is, say, Cr_4C , the formation of carbide will be a function of both the carbon and the chromium concentrations, and therefore the concentration of chromium in the alloy will be important in that it must largely determine the amount of carbon that can be taken into solution before carbide precipitation begins. It might be considered that the more carburizing the atmosphere, the less the concentration of carbide formers which should be present in the alloy, but, since all the alloys tested contained at least 13% chromium, it is doubtful whether the alloys of lower chromium concentration have any marked advantage over the others in this respect. How the presence of nickel rather than of iron affects the precipitation of carbides has not been definitely established, but it may be seen by comparing Figs. 11–14 (Plate LXXXI) with Figs. 21–24 (Plate LXXXIV) that the re-solution of carbides when the carburized materials are reheated to 950° C. and quenched is most marked in the 65 : 15 : 20 alloy; this might be expected in view of the lower concentration of chromium in the alloy, but it is also possible that a nickel-iron-chromium alloy can contain more carbon in solution at 950° C. when the iron concentration is increased at the expense of the nickel. This would result in an iron-containing alloy resisting corrosion in an atmosphere of carbon potential sufficient to give rise to carbide precipitation in an iron-free alloy.

Probably the most important factor in causing corrosion is the preferential precipitation of carbides along the grain boundaries instead

of general precipitation throughout the grains. If an alloy develops grain-boundary precipitation of carbides, the later diffusion of oxygen along the grain boundaries will convert these carbides to oxides. Hence grains which themselves may be resistant to corrosion will be "picked-out" by oxide penetration down the boundaries and rapid corrosion of the alloy in depth will occur. On the other hand, if the precipitation of carbides is not primarily confined to the grain boundaries, the depth of the oxide layer should not increase so rapidly. In the latter case, if the concentration of chromium at the metal-oxide/metal interface is low and if the precipitation of the chromium carbides depends upon the concentration of both the chromium and the carbon, then it is to be expected that as the oxide film grows, so the concentration of chromium around the chromium carbide particles near to the oxide layer will diminish. The chromium carbide particle should, therefore, redissolve although the concentration of carbon in solid solution is high, and chromium is thereby afforded for the replacement of that removed by oxidation. It naturally follows from this reasoning, that the maximum concentration of chromium in solution, near to the surface, can never exceed the definite amount which is controlled by the carbon in solution and hence by the "carbon pressure" of the atmosphere. Under these conditions the material will have its oxidation-resistance diminished to that of an alloy lower in chromium concentration. Such a mechanism of carbide formation and re-solution would explain the "white band" which is observed beneath the oxide layer and above the carbide layer in the corroded materials. The variation of the concentration of oxygen, chromium, and carbon *in solution* near the edge would then be of the type shown in Fig. 44 (Plate XCI).

The restriction of intergranular penetration of carbon is a possible result of the addition of small quantities of elements such as silicon and titanium. For example, alloy No. V does not exhibit preferential intergranular precipitation. The presence of such elements in solid solution in an alloy may also increase the activity of carbon in solution, resulting in a decreased carbon uptake in an atmosphere of fixed carburizing potential as compared with the uptake of a similar alloy to which no additions have been made. In this connection it is interesting to note that Darken ¹⁴ has reported on the increased activity of carbon in iron-silicon alloys above that in iron itself.

VI.—DECARBURIZATION OF CARBURIZED ALLOYS.

In order to determine how the oxide film affected the ingress of carbon, three nickel-chromium alloys were given a further treatment.

These alloys were Nos. KHC, KHG, and KHI (Table II), two of which were similar to previous alloys, but the third of which was of a new composition. Bars of 1 in. dia. and about 3 in. long were turned down to 0.9 in. After being degreased and weighed they were treated in very dry hydrogen plus 3% propane for 75 hr. at 1000° C. After this experiment the alloys were of good appearance and only slightly sooted. The specimens were then lightly brushed to remove any superficial soot and weighed. The increase in weight of the bars as a result of the treatment is shown in Table V. Photomicrographs of the edges of these alloys

TABLE V.—*Results of Decarburization Tests.*

Alloy	Depth of Carbides after Carburization, in. $\times 10^{-3}$	Increase in Weight, g./mm. ² $\times 10^{-4}$	Depth of Carbides after Dry Decarburization, in. $\times 10^{-3}$	Depth of Clear Zone at Edge after Dry Decarburization, in. $\times 10^{-3}$	Depth of Carbides after Wet Decarburization, in. $\times 10^{-3}$	Depth of Free Zone at Edge after Wet Decarburization, in. $\times 10^{-3}$
KHC	100	(1) 0.90 (2) 0.94	95	8	95	0.6
KHG	100	(1) 0.79 (2) 0.86	90	6	90	0.5
KHI	40	(1) 0.76 (2) 0.66	45	1	35	0.1

after treatment are given in Figs. 25–27 (Plate LXXXV). These results indicate that the presence of silicon in an alloy does not increase markedly its resistance to carburization in atmospheres which have no oxygen-containing constituent. On the other hand, the results obtained from the previous set of alloys treated in the carburizing atmosphere first used suggest that when an oxygen carrier such as carbon monoxide is present, alloys containing 2% silicon have very superior resistance to carburization.

If the oxide film is a barrier to carbon entry, it is reasonable to expect that decarburization can be retarded by the same barrier. The following experiments were undertaken to confirm this view. The specimens from the above experiment, i.e. Nos. KHC, KHG, and KHI in the carburized condition, were treated in wet hydrogen (2.5% H₂O) for 80 hr. The resulting structures are shown in Figs. 28–33 (Plates LXXXVI and LXXXVII). It may be seen that specimens KHC and KHG have been decarburized as expected, but that the carbide particles in specimen KHI are being oxidized *in situ*. Presumably this latter oxidation has been able to occur because of the presence of carbide chains right up to the edge of the specimen. In order to produce and test carburized specimens which did not possess carbide particles right to the edge,

three further samples were treated as follows: Heated in dry hydrogen plus 3% propane for 75 hr., followed by decarburization in dry hydrogen for 15 hr. and then by decarburization in wet hydrogen (2.5% H_2O) for 25 hr. at 1000°C . The approximate case-depths after these treatments are given in Table V. Photomicrographs are given in Figs. 34-42 (Plates LXXXVIII-XC), which show the structures of the alloys after these treatments. The difference in the behaviour of the alloys in the wet as compared with the dry atmosphere is very marked. The reappearance of carbides near the edge must be due to the sealing of the surface by an oxide film, thus allowing carbon to diffuse from centre to edge with subsequent carbide precipitation. Fig. 43 (Plate XC) shows the structure of the carbides at the edge of specimen KHI at the end of the three-stage treatment.

TABLE VI.—*X-Ray Analysis of Oxides Formed on Nickel-Chromium Alloys in Wet Hydrogen.*

Alloy No.	Length of Treatment (hr.) in Wet H_2 (2½% H_2O) at 1000°C .	X-Ray Analysis	
		Crystalline Phases Detected in Oxide Layer	Remarks
KHC	5	Cr_2O_3 —strong $\text{NiO}.\text{Cr}_2\text{O}_3$ —medium	$\text{NiO}.\text{Cr}_2\text{O}_3$ has the usual spinel-type structure.
I	5	Cr_2O_3 —strong A phase of spinel-type structure—weak	The lattice parameters of the spinel phase closely match those of $\text{NiO}.\text{Cr}_2\text{O}_3$, but some replacement of Cr by Fe may have taken place.
IV	5	Cr_2O_3 —strong $\text{NiO}.\text{Cr}_2\text{O}_3$ —medium	The constitution of this oxide layer is very similar to that formed on alloy KHC.
KHG	5	A phase of spinel-type structure	The spinel detected here appears to have roughly the same lattice parameter as $\text{NiO}.\text{Cr}_2\text{O}_3$, but some Cr may have been replaced by Fe atoms.
V	5	Spinel phase similar to KHG	
KHI	5	Cr_2O_3 —strong A spinel phase similar to that of KHG—strong	

In order to investigate further the nature of the oxide film, a set of alloys was treated for 5 hr. in hydrogen plus 2.5% water vapour at

1000° C. This atmosphere was used in preference to air because it was reducing to both iron and nickel at this temperature just as the carburizing atmosphere had been. The structures of the oxide coatings under X-ray examination are given in Table VI, and it will be seen that there is little difference between them and those obtained on alloys Nos. I to V treated in air (Table IV).

The results of the experiments described in this section are not conclusive. The carburization–decarburization tests show that the oxide film formed on a silicon-free nickel-chromium alloy retards the egress of carbon when the alloy is heated in a decarburizing atmosphere. It is considered that the same barrier restricts carbon entry under carburizing conditions, and that the presence of silicon increases the effectiveness of the barrier. It is difficult to believe that carbon can diffuse through the protective oxide layer on nickel–chromium alloys unless there are rifts or faults in this layer. Whether the presence of silicon results in the closure of such rifts or whether its effect is to reinforce the oxide at the metal/metal-oxide interface is not known. However, the X-ray evidence has shown that silicon causes no change in the bulk structure of the oxide and therefore the influence, if any, of the silicon on the condition of the oxide layer must be either at scattered points or over a narrow layer.

VII.—CONCLUSIONS.

(1) The high-temperature corrosion of certain chromium-bearing alloys has been shown to occur in carburizing atmospheres containing combined oxygen, by the simultaneous carburization and oxidation of the alloy.

(2) Carburization leads to a reduction of the effective concentration of chromium in the matrix as a result of carbide precipitation, to an extent dependent upon the carburizing potential of the furnace atmosphere and upon the solubility of carbon in the matrix. The chromium carbides thus formed are susceptible to oxidation, and, when they are present at grain boundaries, rapid intergranular oxidation of the alloy occurs in depth, giving rise to the type of corrosion known as “green rot”.

(3) The presence of approximately 2% silicon in a nickel–chromium–iron resistor alloy is sufficient to prevent carburization in atmospheres containing both carburizing gases and combined oxygen. However, in an oxygen-free and carburizing atmosphere, and in the absence of a superficial oxide film, a similar type of alloy carburizes readily. There is evidence that the presence of 2% titanium confers some resistance to carburization when combined oxygen is present in the atmosphere.

(4) It is suggested that the inhibiting effect of silicon is associated with the nature of the oxide film on the alloy. This effect may be either confined to the metal/metal-oxide interface in the form of a barrier film rich in silica, or associated with the ability of silica to seal rifts in the oxide layer, through which carburization of alloys low in silicon takes place.

(5) The addition of iron to a nickel-chromium alloy also may increase its resistance to "green rot". It is considered that this is due, in the main, to the greater solubility of carbide in such alloys within the range of temperatures used in the experimental investigation.

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A METHOD FOR ASSESSING THE RELATIVE CORROSION BEHAVIOUR OF DIFFERENT SEA-WATERS.* 1234

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SYNOPSIS.

Experience accumulated over many years has shown that the corrosive attack of sea-waters on copper-base alloys varies considerably because of factors inherent in the sea-waters that are not easily revealed by ordinary chemical tests. The corrosive nature of a sea-water varies with the season of the year and also with the time during which the sample is stored before use. These variations in the corrosiveness of different samples make it very desirable that some indication should be given of the corrosiveness of the sea-waters when comparing corrosion experiments carried out in this medium. In view of this a simple test, known as the Copper Corrosion Index determination (C.C.I.), has been developed to gauge the corrosiveness of any particular sample of sea-water. It consists in immersing a piece of copper sheet of given area in the sample of sea-water and estimating the amount of copper dissolved in 22 hr. under standard conditions.

The paper describes in detail the technique of the test, its use for estimating variations in the corrosiveness of sea-waters, and its value in accounting for lack of reproducibility in sea-water corrosion tests on copper-base alloys.

I.—INTRODUCTION.

THE difficulties of obtaining reproducible results from corrosion experiments carried out in sea-water are well known.

Experience over two decades of testing copper-base alloys for resistance to attack by sea-water in the B.N.F.M.R.A. laboratories has shown that the attack will vary as a result of factors inherent in the sea-water, quite apart from any physical variation in the materials under test. Sea-water from the open sea normally produces much milder types of corrosion than inshore waters, which, on occasion, cause exceptionally severe attack. The factors controlling these variations are the locality from which the water sample is taken, the time of year at which it is collected, and the time which elapses between collection and use.

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Corrosion experiments conducted in a single sample of sea-water or artificial sea-water can, therefore, lead to incorrect estimations of service behaviour, and the development of an alloy for use in sea-water needs to be carried out in a variety of waters.

In view of the variable behaviour of sea-water there is clearly a need for a simple test capable of giving a measure of the corrosiveness of a sea-water sample. Such a method would facilitate the correlation of the results of different workers using different sea-water samples and probably different types of corrosion test.

The pH and saline composition of sea-water are fairly constant, though they vary more in inshore locations than in the open sea, and experience has shown that such variations as occur are of minor importance. Of much greater effect are the small amounts of contaminating substances produced by biological activity. It must be remembered that sea-water is a biological entity not unlike soil, and its organic nature must be taken into account. Normal water analysis is, therefore, of only limited value in the problem of estimating the corrosiveness of sea-water.

It has been shown elsewhere that various organic substances produced by bacterial metabolism and other life processes can accelerate corrosion reactions,¹ but it is unlikely that all organic matter in sea-water will accelerate corrosion, and indeed some may inhibit it. The degree of attack will, therefore, probably depend upon the balance between accelerators and inhibitors. Thus, methods of assessing the total organic matter will not be a reliable guide to the corrosive nature of sea-water.

One approach to the problem was by the use of the polarograph, which had proved successful in estimating small quantities of corrosion accelerators added to sea-water. However, little correlation was found between the corrosiveness of natural sea-water samples and the polarograms obtained from them, and it was suspected that many other substances present, besides those affecting the corrosiveness of the waters, were causing variations in the polarograms.

The problem has also been approached by the study of electrode potentials and polarization curves, but experiments with a variety of electrodes in different sea-waters have not enabled electrochemical measurements to be correlated with the corrosiveness of the water. In a previous paper by the author,¹ it was shown that the presence of organic sulphur compounds in sea-water could be responsible for considerable variations in its corrosive behaviour. One of the tests used to estimate the accelerative effect of cystine additions was to determine the amount of copper passing into solution from a specimen of O.F.H.C.

copper of standard surface area. These results (see Fig. 4 of previous paper¹) showed that *in the earlier stages* of such a test, the amount of copper going into solution increased progressively with increase in the amounts of cystine added. This suggested that the "solution" by sea-waters from copper specimens of equal areas under standardized conditions might be used to assess the corrosive character of a sea-water.

This is the basis of the test which has been called the Copper Corrosion Index determination. This paper describes the method of determining the Copper Corrosion Index, the variation of this index with storage and aeration of sea-water, and the correlation of the corrosion of certain condenser-tube alloys with the index, and discusses the significance of the results when analysed statistically.

II.—GENERAL EXPERIMENTAL PROCEDURE.

Sheets of copper of standard surface area are hung in three beakers containing equal volumes of the sea-water to be tested. After aeration by a jet of air for a fixed time the copper in the corrosion products in each beaker is determined either volumetrically by a standard method, or colorimetrically by a method specially developed at the B.N.F.M.R.A. (see Section III (d) (ii)).

The Copper Corrosion Index (C.C.I.) is the average amount of copper in milligrammes corroded from the three specimens under these conditions, allowance being made for any copper initially present in the sea-water sample.

III.—STANDARDIZED EXPERIMENTAL PROCEDURE.

(a) *Conditions of Test.*

Triplicate 350-c.c. samples of the sea-water are placed in 600-c.c. beakers and immersed in a thermostat maintained at $20^{\circ} \pm 0.5^{\circ}$ C. The water is aerated and stirred by means of glass jets (see below), calibrated to deliver 500 ± 10 c.c. of air/min. when air is supplied at a pressure of 20 lb./in.² After 4 hours' aeration, specimens cut from 16-gauge O.F.H.C. copper sheet to give 0.25 dm.² (approx. 5×2.5 cm.), with a hole of 2 mm. dia. in the centre of one end, are hung in the beakers on glass stands so that the specimens are always the same distance below the water line (Fig. 1). To avoid impingement of air on the specimens, the jets and stands supporting the specimens are placed at opposite sides of the beakers. The copper sheets are left in the aerated and stirred sea-water for 22 hr. This period was chosen on the basis of previous results (Fig. 4 of the previous paper¹) and because 22 hr. is a convenient time for successive runs using the same jets, i.e. one run can be completed and another begun each day.

At the end of the period the copper sheets are removed, and any corrosion products on them washed into the beaker by a jet of distilled water, and the total copper in the beakers estimated. It is also possible to obtain the C.C.I. by determining the loss in weight of the specimens, but this is not recommended owing to the possibility of film formation on the copper specimens.

(b) *Preparation of Specimens.*

The specimens are first cleaned with 100x emery cloth to remove surface films. They are then abraded on 240x emery cloth, using A.R. benzene as a lubricant.

The surfaces must be perfectly clean, and any emery remaining after the final cleaning is removed by washing in benzene, followed by three washes in pure dry acetone.

The copper sheets are then immediately hung on the glass stands and immersed in the beakers of sea-water.

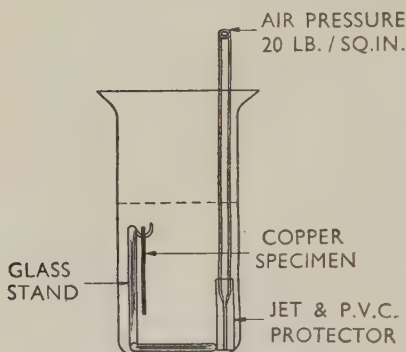


FIG. 1.—Arrangement of Specimen in Beaker.

(c) *Details of Apparatus.*

(i) *Jets.*

The jets are made of capillary tube of 2 mm. bore drawn out at one end to a fine jet of approximately 0.125 mm. dia. This gives a tapered jet which is readily adjusted to the correct rate of delivery by grinding on a glass plate, using fine emery powder. In order that the jets may be fairly robust the overall length of the drawn-out portion should not exceed 1.5 cm. and should be protected by a sleeve of "P.V.C." tubing approx. 3 cm. long, fitted over the main tube. Calibration is sufficiently accurate if done by standard displacement methods, but it is essential that after preparation the jets should not be used for about three weeks, as considerable alterations can occur immediately after drawing.

(ii) *Air Supply.*

Air should be supplied at 20 ± 0.5 lb./in.² without undue pulsation. In order to prevent stoppage of the jets and contamination of the sea-water, the air must be filtered. A suitable method is to use an iron cylinder about 2 in. in dia. and 2 ft. long, capped at both ends and

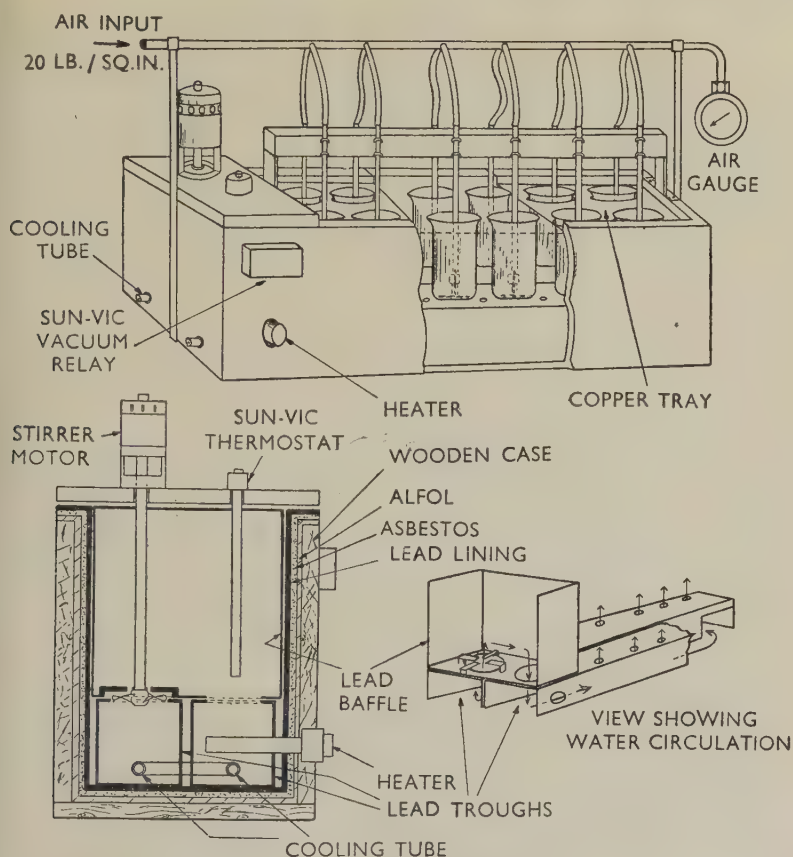


FIG. 2.—Diagram of Apparatus for Copper Corrosion Index Determination.

loosely packed with cotton wool for three-quarters of its length. The air, led into the cylinder about 6 in. from the bottom, is filtered through the cotton wool and taken out at the top. The bottom six-inch portion acts as a trap for moisture, which is removed at regular intervals through a tap at the bottom of the cylinder. If the air supplied is quite dry, salt will form in the capillaries and stoppages occur. This is easily obviated by bubbling the air through water before filtration.

(iii) *Thermostat.*

This should maintain the beakers at $20^{\circ} \pm 0.5^{\circ}$ C. with no greater variation between the ends of the bath. The thermostat should also be provided with a water-cooling coil for use in the summer months (Fig. 2).

(d) *Determination of Copper.*

At the end of the test the beakers usually contain a little copper in the basic state, some of which adheres to the stand used in the test. With the stand still in position, 3 c.c. of conc. HCl are added, and the contents of the beaker are warmed slightly to dissolve the basic material. The glass stand is removed and rinsed down, as are the sides of the beaker. The solution is well stirred and the copper is then determined by method (i) or (ii) below.

(i) *Volumetric Determination of Copper.*

After separation as sulphide, the copper is determined by the standard iodometric method of Haën-Low.²

(ii) *Absorptiometric Determination of Copper.*

The acidified solution is diluted to 400 c.c. and mixed well. To a 5-c.c. aliquot are added 10 c.c. of ammonium citrate solution,* followed by 10 c.c. of gum arabic solution,† 40 c.c. of water, and 20 c.c. of 0.880 *d* ammonia, with vigorous stirring after each addition. Finally, 10 c.c. of "carbamate" solution‡ are added, with uninterrupted stirring throughout. The mixture is diluted to 100 c.c.

The absorption is then measured on a "Spekker" absorptiometer, using a 2-cm. cell, Chance OB2 + Wratten 50 filters, and a drum setting of WATER TO WATER—1.0.

A blank determination is carried out, using all reagents but omitting the sample aliquot. The difference in readings between the blank and the sample is referred to a previously prepared calibration graph to determine the copper content.

IV.—STATISTICAL CONSIDERATION OF THE FIGURES OBTAINED IN THE C.C.I. ESTIMATIONS.

The C.C.I., as explained above, is obtained by averaging the amount of copper found in each of three beakers. Estimations on well over 500 different samples of natural sea-water have shown the C.C.I. to vary between about 3 and 30.

In the preliminary stages of development of the test, before sufficient results were available for statistical analysis, it was evident

* 500 g. of A.R. citric acid are covered with water and 500 c.c. of 0.880 *d* ammonia added a little at a time, the solution being cooled whilst the addition is being made. The solution is boiled and then filtered through a 540 Whatman paper on a Buchner funnel, cooled, and diluted to 1 litre.

† 10 g. of selected gum arabic crystals are dissolved in hot water and diluted to 1 litre and filtered as above.

‡ 1 g. of sodium diethyldithiocarbamate dissolved in 1 litre of distilled water.

that the scatter within the groups of three increased with increase of C.C.I. It was therefore important as soon as sufficient figures were available, to subject them to statistical analysis to determine what differences in C.C.I. could be considered significant.

It was first of all necessary to group the sea-waters into some arbitrary categories; 428 sets of triplicate estimations were therefore arranged in the following five categories according to their respective averages (C.C.I.): below 5, 5-10, 11-15, 16-20, and over 20.

The significant difference for each category was then calculated by the method described by Hartley ^{3, 4} for testing the homogeneity of a set of variances.

The test was applied to two sets of groups of three taken at random from the highest and the lowest categories (below 5 and over 20). It appeared that the variances could be considered homogeneous within each of these categories. As these two extreme categories were homogeneous, it was considered justifiable to conclude that the intermediate categories were of a similar nature. The homogeneity of the sets of variances having been shown, it is considered statistically legitimate to accept as significant any figure which is greater than twice the standard deviation for each group. On this basis the significant differences between the averages (C.C.I.) in each category are shown in Table I. For practical purposes they have been rounded off at values slightly above the theoretical figures. Thus, two sea-waters having C.C.I. values of 19.0 and 20.0 would not be considered significantly different, but two sea-waters with C.C.I. values of 5.0 and 6.0 would be considered of different degrees of corrosiveness.

TABLE I.—*Calculated Significant Difference Figures for Averages (C.C.I.) in Each Category with Suggested Practical Values.*

Category	Below 5	5-10	11-15	16-20	Over 20
Significant difference . . .	0.8	1.0	1.9	1.7	2.0
Practical value . . .	1.0	1.0	2.0	2.0	2.0

V.—PRACTICAL USE OF THE COPPER CORROSION INDEX.

(a) *Variations of C.C.I. on Carboys of Sea-Water on Delivery and Storage.*

Sea-water used for corrosion tests, collected from various localities, is often thought to be a much more stable fluid than is, in fact, the case. Many C.C.I. estimations have been made, over the last few years, on carboys of sea-water as received into the B.N.F.M.R.A. laboratories in London. A selection of these estimations is given in

Table II, including some figures for the natural copper content of several of the waters. Not only do the C.C.I. figures of the carboys vary from collection to collection, but also differences are found between carboys received on the same date and presumably filled within a few minutes of each other. The natural copper content also varies from time to time.

TABLE II.—*Copper Corrosion Indices of Sea-Waters from Various Localities Received into the Laboratory, in Carboys, During 1943-48.*

Carboy No.	C.C.I.	Natural Copper Content, mg./l.	Remarks
40/43	3.6	...	} Carboys collected at same time. Note variation.
41/43	5.0	...	
53/44	6.6	0.03	} Carboys collected at same time.
55/44	5.6	0.03	
56/44	5.3	0.03	
62/44	5.5	0.27	
71/45	6.7	0.10	} Carboys received on same date. Note variations.
72/45	4.2	0.10	
73/45	5.6	0.10	
S/1/46	10.9	0.03	
A/46	8.3	...	
F/47	3.5	0.12	
O/48	7.9	...	
R/48	7.6	...	
A/48	9.4	...	
E/48	9.6	...	

Note: The C.C.I. of 3% sodium chloride solution is approx. 4.5.

It is unfortunate that, owing to difficulties of collection or war-time restrictions, no figures are available for a single locality covering several seasonal cycles. Therefore no figures can be quoted to show conclusively the variation in C.C.I. with season. However, it is often found that waters collected in the early spring and summer develop a greater corrosiveness than those of the autumn and winter months.

Sea-waters received at the laboratory are often stored before use, and the effect of storage on their corrosiveness has been investigated (see Table III).

Table III shows that there are appreciable variations in the C.C.I. of carboys of sea-water during storage. The water in carboy 42 nearly doubled its corrosiveness towards copper in six weeks, while the waters

TABLE III.—*Copper Corrosion Indices of the Waters of Four Carboys (Nos. 42, 46, 52, and 57) Stored in the Laboratory for Varying Periods (Stagnant between 15° and 20° C.).*

No. and Age of Carboys	Copper Corrosion Index	No. and Age of Carboys	Copper Corrosion Index
42. As recd.	3.9	52. As recd.	...
3 weeks	5.9	2 weeks	5.5
5 "	6.4	7 "	5.9
6 "	7.2	9 "	5.3
		11 "	6.4
46. As recd.	7.3	57. As recd.	6.6
3 weeks	6.8	4 weeks	6.3
5 "	5.3	8 "	4.3
6 "	4.7	12 "	3.7

in carboys 46 and 57 became less corrosive, and that in carboy 52 remained more even in its behaviour. These figures confirm the experience of the B.N.F.M.R.A. Corrosion Laboratory that storing a sea-water for a few weeks alters its corrosion behaviour, but in no predictable manner.

Determinations on a carboy of sea-water which was continuously aerated for some weeks showed that irregular variations of C.C.I. occurred (see Table IV). About half-way through the test a small quantity of fish

TABLE IV.—*Variations in the Copper Corrosion Index of a Carboy of Sea-Water Kept Under Continuous Aeration for About Five Months.*

Age of Carboy	Copper Corrosion Index	Age of Carboy	Copper Corrosion Index
24 hr.	6.1	90 days	9.3
14 days	2.9	93 "	12.7
28 "	4.0	111 "	9.3
42 "	3.0	114 "	9.8
66 "	4.4	139 "	4.8
84 "	Fish skin added to water	142 "	7.4

skin was added to the carboy and allowed to decompose, with consequent considerable increase in bacterial activity; a rapid rise in C.C.I. occurred, followed by a fall and then a return to irregular variation.

(b) *The C.C.I. of Sea-Water Used in the Jet-Impingement Apparatus.**

Since the development of the technique described in this paper, regular estimations of C.C.I. are made at the beginning and end of the

* The assessment of condenser-tube alloys is usually carried out in the jet-impingement apparatus developed by May.⁵

28-day periods of the jet-test runs and also at selected intervals during the runs. Table V gives a selection of figures obtained during such experiments, showing that the corrosive character of the sea-waters varies throughout the period of the runs.

TABLE V.—*Copper Corrosion Indices of Jet-Test Waters.*

Jet-Test Run	Source of Water	C.C.I. Estimation				
		Start	7 days	14 days	21 days	28 days
T/45	Colwyn Bay	7.2	10.4	11.8	11.6	12.0
V/45	"	7.3	12.8	11.1	12.5	14.8
X/45	"	9.0	10.2	12.6	11.9	12.5
F/46	Chichester Harbour	13.1	14.8	15.1	16.8	22.4
M/46	"	8.3	5.2	5.7	4.5	4.4
J/48	"	26.8	11.5	11.6
F/47	Irish Sea	3.5	4.1	3.6	5.0	3.9
J/47	"	5.7	5.1	4.5	7.3	6.2
L/47	"	6.7	8.9	5.6	8.8	9.5

The Colwyn Bay waters show an increase in C.C.I. during the runs, the Chichester Harbour waters are very irregular, and the Irish Sea waters are generally lower in C.C.I. and do not show wide variations. These results are typical of the behaviour of the waters from each locality, although the waters do not invariably behave in the manner described. It is usual for the C.C.I. of waters from the open sea to be less than 10 on receipt and to remain very steady during test, and the degree of attack produced is usually small. With inshore waters, however, the C.C.I. during the run is usually very irregular, irrespective of the value on receipt. When the C.C.I. rises during the run, pitting attack usually becomes more marked.

C.C.I. estimations made to study the effect of temperature changes during jet-test runs have shown that there is close correlation between C.C.I. and change of temperature. The alteration in C.C.I., however, appears to lag behind the temperature change by about 4–6 days. This suggests that temperature variations affect the biological activity in natural sea-water and hence the corrosiveness.

(c) *Correlation Between C.C.I. Values and the Behaviour of Some Condenser-Tube Alloys in the Jet-Impingement Apparatus.*

Despite the variation in the corrosiveness of sea-waters during storage and during corrosion tests, it is possible to correlate, to some extent, the behaviour of the standard condenser-tube alloys in the jet-impingement apparatus with the C.C.I. of the sea-waters.

Corrosion in sea-water is particularly affected by the formation

and breakdown of films, and the rate of attack often depends upon the balance between suppression of attack by film formation and acceleration of attack due to film breakdown.

In general, with a low C.C.I. value there is little filming of materials in the jet test, rarely any pitting action, and impingement attack is shallow and widespread. Film formation and pitting action tend to increase as the C.C.I. increases, but attack at the jet area may not directly follow the increases in contamination. In waters of high C.C.I. value, filming is often considerable and can result in the stifling of attack (see Run U/45, Table VII). On the other hand, a water of high C.C.I. value may produce an unstable film which breaks down at the jet area and causes severe attack (see Run Q/45, Table VII).

Further, pre-exposure of an alloy in sea-water can affect its subsequent behaviour in the jet test. Thus, immersion in water of a high C.C.I. value may cause development of attack of the type to be expected in a contaminated water when the alloy is subsequently tested in the jet test in water of low C.C.I. value.

TABLE VI.—*The Corrosion Behaviour of Arsenical Copper in the Jet-Impingement Apparatus in Sea-Waters of Different C.C.I. Values.*

Run No.	Copper Corrosion Index					Attack at Jet. Depth and Type	General Appearance after Test
	0 days	7 days	14 days	21 days	28 days		
P/45	6.2	4.9	5.9	6.8	5.6	(0.10 mm.) Very widespread impingement, no concentration of attack.	Very little filming, considerable general solution of copper all over surface.
R/45	5.8	6.3	8.6	6.3	7.4	(0.16 mm.) Very widespread impingement, slight concentration of attack.	More filming than in Run P/45 and area of attack at jet less in dia.
T/45	7.2	10.4	11.8	11.6	12.0	(0.48 mm.) Considerable concentration of attack in jet area.	Dark flaking film much heavier than above, with surface attack beneath.
W/45	12.2	15.3	12.8	12.1	14.6	(0.58 mm.) Attack at jet concentrated into deep pit.	Heavy flaking film, with severe surface attack beneath. Attack in jet area concentrated by highly cathodic film early in run.

In general, corrosion under impingement conditions increases with increase in C.C.I. value. This is well shown in Table VI, which gives the attack on arsenical copper in the jet-impingement apparatus, using waters of four different C.C.I. values.

In Table VII is shown the behaviour of 70 : 30 (0.04% iron) cupro-nickel in waters of varying corrosiveness, and here again increase of attack corresponds roughly with increase in C.C.I. value.

TABLE VII.—*The Corrosion Behaviour of 70 : 30 (0.04% Iron) Cupro-Nickel Alloy in the Jet-Impingement Apparatus in Waters of Different C.C.I. Values.*

Run No.	Copper Corrosion Index					Depth of Attack at Jet, mm.
	0 days	7 days	14 days	21 days	28 days	
Z/48	7.9	5.0	4.9	0.04
V/48	5.9	7.5	8.6	0.05-0.08
H/48	7.9	8.4	9.2	0.10
AB/48	7.7	8.2	7.4	0.15
S/48	11.4	10.2	5.5	0.20
Q/45	6.6	13.7	14.8	14.5	15.3	0.59
V/45	7.3	12.8	11.1	12.5	14.8	0.60
U/45	5.9	6.3	12.0	13.3	15.6	0.09 *

* Attack almost completely stifled by heavy, shining, glass-like film.

These results illustrate the difficulties encountered in corrosion testing in natural sea-waters. The depth of attack at the jet on this single alloy varied from 0.04 to 0.60 mm. as a result of differences in the waters used. Clearly, in the absence of some means of assessing the corrosiveness of a sea-water sample, little significance can be attached to variations between the behaviour of one alloy and another when tested in different sea-waters. An exception to the general increase of attack with C.C.I. in Table VII, is run U/45 in which comparatively little attack occurred in spite of a high C.C.I. value in the later stages. Examination of the specimen revealed a heavy protective film. Abnormal behaviour of this kind, which sometimes occurs in contaminated waters, is easily recognized by low-power microscopical examination, and the possibility of such occurrences has to be borne in mind when assessing the corrosiveness of sea-waters by the C.C.I. value.

It is found that some alloys are much more susceptible to changes in C.C.I. than others. Thus resistant materials such as aluminium brass and 70 : 30 (0.5% iron) cupro-nickel alloys behave well in all waters, except those which have abnormally high C.C.I. (20 or more),

usually associated with the presence of hydrogen sulphide, when severe pitting attack is liable to occur. On the other hand, less-resistant alloys, such as Admiralty metal and 70 : 30 (0.04% iron) cupro-nickel, are very sensitive to change in C.C.I. This is shown in Table VIII,

TABLE VIII.—*The Corrosion Behaviour of Various Copper-Base Alloys in the Jet-Impingement Apparatus in Sea-Water of Different C.C.I. Values.*

Duplicate specimens except where stated.

Run No.	C.C.I.*					Depth and Type of Attack at Jet Area		
	0 days	7 days	14 days	21 days	28 days	Alloy 70 : 30 (0.04% iron) Cupro-nickel	Alloy 70 : 30 (0.5% iron) Cupro-nickel	Alloy 90 : 10 (0.7% iron) Cupro-nickel
N/47	9.6	12.8	12.8	0.24 and 0.13 mm. Impingement attack and pitting under heavy blistered film.	No attack at jets, considerable deep pitting on surface under film. Some blistering of film.	Specimens penetrated in 10 days by impingement, holes then enlarged by oxide attack.
P/47	8.0	11.8	5.2	Impingement attack almost absent, few pits compared with N/47. Some blistering of films.	No attack at jets, fewer pits than N/47, some blistering of film.	Slight impingement but more attack at jets and more blistering of film than in 70 : 30 alloys.
R/47	13.7	17.6	...	0.38 and 0.74 mm. Impingement attack and considerable pitting under heavily blistered film.	No attack at jets but much blistering and pitting.	Specimens penetrated, similar to Run N/47.
A/48	11.8	9.2	8.8	Single specimen. 0.11 mm. Impingement attack but less blistering than Run P/47.	Single specimen. No significant impingement attack but much blistering.	0.30 and 0.36 mm. Considerable impingement attack associated with oxide pitting.

* C.C.I. figures were not obtained at all periods in these runs, as efforts were being made to see if it were possible to estimate a sea-water's behaviour in the jet test in less than five estimations. P/47 can be considered the cleanest water followed by A/48, N/47, and R/47.

where in four runs in waters of varying C.C.I. two 70 : 30 cupro-nickel alloys containing respectively 0.5% and 0.04% iron were tested. The high-iron 70 : 30 cupro-nickel, an alloy known to behave excellently in service, was not appreciably attacked at the jet in any run, though a tendency to attack by pitting action became more evident as the C.C.I. increased. The depth of impingement attack on the low-iron alloy, on the other hand, varied from virtually nil to 0.74 mm. as the C.C.I. increased, and the tendency for film breakdown also increased.

The all-round resistance of an alloy to corrosion by sea-water can therefore be properly assessed only by testing in different sea-waters. This is also well shown in Table VIII, which gives results for a 90 : 10 cupro-nickel alloy containing 0.7% iron, tested in four different water

samples. If this alloy had been tested only in waters of the type used in Run P/47, a completely erroneous estimation of its good behaviour under impingement conditions would have been obtained. Attack on this alloy, as on the 70 : 30 (0.04% iron) cupro-nickel alloy, increased as the C.C.I. increased.

(d) *Attempts to Control the C.C.I. of Jet-Impingement Apparatus Tests.*

It has been known for many years that the addition of iron salts to condenser cooling waters renders them less corrosive.⁶ Preliminary attempts have been made to control the behaviour of sea-water during jet-impingement tests by making such additions during the test. The addition decreased the C.C.I. considerably, and caused more widespread and less dangerous attack at the jet area. There was also a tendency for the waters to remain more constant during the runs, but in some cases this effect was not permanent. The effect of the addition of iron salts is probably due to the absorption of the available organic matter by the iron salts; this has been demonstrated experimentally in the case of cystine additions to sea-water, in which the removal of cystine by iron salts has been followed polarographically.

VI.—CONCLUSIONS.

The degree of contamination of a sea-water can be estimated by the Copper Corrosion Index (C.C.I.) based on the amount of copper corroded, under standard conditions, from a standard area of O.F.H.C. copper sheet, a rise in C.C.I. values being usually associated with increased attack.

C.C.I. determinations show that samples of sea-water are liable to vary in corrosiveness, at time of receipt, during storage, and during jet-impingement tests. Increase in biological contamination and rise in temperature are two of the factors causing these variations.

C.C.I. determinations have shown that variations in the degrees of attack on a given alloy tested at different times are primarily due to variation in the corrosiveness of the sea-waters used.

Sea-waters with high C.C.I. values tend to form films on copper-base alloys which may stifle corrosive attack or cause highly localized corrosion. High C.C.I. values are also often associated with films that blister and increase of attack at "shielded areas". In such cases low-power microscopical examination should supplement the C.C.I. determinations.

Sea-waters of low C.C.I. values give less visible evidence of film

formation on copper-base alloys and cause widespread attack on alloys liable to undergo impingement attack in service, but little or no attack on alloys known to be resistant in service.

The evaluation of a series of copper-base alloys for resistance to attack by moving, aerated sea-water can best be carried out in sea-waters in the C.C.I. range 12-18. If the C.C.I. value is outside this range, differentiation is often difficult owing to negligible attack, stifling by heavy films, or excessive attack on all materials.

Previous exposure of copper-base alloys to water of varying C.C.I. values can affect their subsequent corrosion behaviour.

Copper-base alloys insensitive to variation in C.C.I. value usually behave well in service and vice versa.

The C.C.I. value of a water can be decreased by the presence of iron salts in the water, but experiments show that this effect may not be permanent.

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STATIC MODELS OF DISLOCATIONS.*

1235

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SYNOPSIS.

A model is described with which various crystal lattices can be built. These can be deformed elastically and dislocations introduced. With this model the geometry of the motion and arrangement of dislocations of various types, and certain results of the elastic theory of dislocations, can be demonstrated. Selected examples of dislocations in a simple cubic lattice are considered in order to illustrate the scope and limitations of the model.

I.—INTRODUCTION.

A THEORY of the plasticity of crystals put forward by Taylor,¹ Orowan,² and Polanyi³ postulates that slipping occurs by the propagation of lines of discontinuity in the lattice which have been named "dislocations". A dislocation is defined as the type of line discontinuity lying in the slip planes of a crystal that separates a region which has slipped from one which has not. Such discontinuities must arise if slipping occurs by a process of steady extension of regions of local slip and not simultaneously over the whole slip plane, but they may be produced by other processes. The extreme uniformity of conditions required for simultaneous slip suggests that it is unlikely to occur and provides an argument for the dislocation postulate.

Bragg and Nye⁴ have described a dynamic model of a two-dimensional close-packed crystal, in which the atoms are represented by small bubbles assembled in rafts on the surface of a liquid. When a sufficient shear stress is applied to such a bubble-raft, slip is seen to occur by the propagation of dislocations. A three-dimensional model is obtained by making rafts containing several layers of bubbles.

In the present paper an account is given of a simple static three-dimensional model in which the internal irregularities in a crystal caused, for example, by dislocations or foreign atoms, may be represented. Only dislocations are discussed here, and for simplicity a model of a simple cubic lattice is used. The model shows how combinations of dislocations arise naturally from simple physical operations, and it is useful in studying the geometry of the more complex dislocation arrays. Certain features of the elastic strain fields round the dislocations and of the interaction forces which arise from them are also shown qualitatively

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by the model. To illustrate its scope and limitations, a number of simple examples are considered; clear photographic illustration becomes increasingly difficult with the more complicated arrays, although the model itself shows the phenomena clearly.

II.—THE MODEL.

The model is made from wooden balls 1 in. in dia., each drilled with twenty-six holes in the direction of the tetrad, triad, and diad axes of symmetry of a cube; such balls are in common use for models of crystal structures. They enable cubic and hexagonal structures to be made and are thus suitable for models of metallic crystals. To obtain a model of an elastic solid in which dislocations can be made, the balls are joined not by rigid rods, but by short lengths of steel spring; flexible curtain rod is convenient and readily available. The model is thus itself a multiply-connected body made up of a system of elastic rods rigidly joined at their ends. The states of equilibrium possible in such a system have been discussed by Volterra.⁵ This model represents a structure which is very anisotropic elastically because the spring from which the rod is made is easily bent but is difficult to extend or compress. Young's modulus for the model is much less in the [110] direction than it is in the [100] direction. Also, under a hydrostatic stress which it will withstand without disintegrating, the model shows practically no dilatation. These elastic properties influence the elastic strains observed round dislocations in the model. It will be noticed in the photographs that slight irregularities occur in the model: these are easily distinguished from the larger effects of elastic distortion. When the model is deformed, the bonds normally assume a curved form, and in regions of high compression, buckling occurs.

III.—EDGE DISLOCATIONS.

(a) *Introduction.*

The passage of a positive edge dislocation (the type originally proposed by Taylor) across a model of size $3 \times 3 \times 6$ lattice spacings is shown in Figs. 1-4 (Plate XCII), the model being viewed along the dislocation line. The slip plane passes horizontally through the centre of the model roughly perpendicular to the plane of the paper, and slip of one lattice spacing (λ_0) is represented by disconnecting rows of bonds across the slip plane in the region where the slip is to occur, and re-joining each row above the slip plane, not to the corresponding row below, but to the one adjacent to it. Thus in Figs. 1-4 increasing amounts of the left upper half of the model have slipped to the right

one spacing with respect to the lower half, and the edge dislocation always appears naturally as the boundary region between the slipped and unslipped material. The "strength" of the dislocation is defined as the difference in amount of slip on the two sides of the line of dislocation—in this example it is λ_0 . The series of positions shown can be obtained if the dislocation is moved by disconnecting and connecting successive lattice rows. The process of the spread of the slip across the slip plane is thus that of the motion of the dislocation line—the boundary of the slipped region—across the slip plane. After the position of Fig. 4, further movement of the dislocation to the right causes it to pass out of the model, leaving a perfect lattice in its wake, but with the upper half displaced to the right of the lower by one lattice spacing—the strength of the dislocation. The slip can be continued by introducing successive dislocations from the left. Obviously this type of dislocation can be made by introducing an extra vertical "half-plane" above the slip plane. If the model is inverted, the extra "half-plane" is taken below the slip plane, and a negative edge dislocation is obtained. The motion of the negative type from right to left produces the same slip as that of the positive type from left to right (invert Figs. 1–4).

Considerable force has to be applied to the model in order to distort it sufficiently to introduce the dislocation; once there, however, the dislocation can be moved easily across the slip plane. This shows that large changes of elastic energy are involved in the formation of dislocations, but much smaller ones in their motion. Obviously only very small movements of the lattice rows accompany unit movement of the dislocation. The signs of the elastic shears round the dislocation are shown, and the state of compression immediately above the slip plane, indicated by occasional buckling, is apparent on handling the model. A state of tension exists immediately below the slip plane; this can be shown if the two lattice rows immediately below the dislocation line are disconnected, for they then spring apart with a considerable release of strain energy.

(b) *Effects of Surfaces.*

Fig. 5 (Plate XCIII) shows an edge dislocation in a position intermediate between that of Figs. 3 and 4. It is convenient, since the edge dislocation repeats in form indefinitely along its line, to use a model extending for only one lattice spacing in this direction. Both the bonds 2–4 and 2–5 are absent; if the former are introduced, the dislocation lies above 2–3; and if the latter, it lies above 1–2. On account of the asymmetry, less distortion of the model is required to join 2–4 than to join 2–5. Thus the energy of the model is reduced if the dis-

location moves from 1-2 to 2-3 (or from the position in Fig. 3 to that in Fig. 4), and a force acts on the dislocation in the direction of the right-hand surface. By considering the asymmetry of intermediate positions of the dislocation farther from the surface, it can be seen from the models that this force increases in magnitude as the surface is approached. The force arises because the dislocation is in an elastic solid which is bounded by surfaces at a finite distance. Koehler⁶ has shown that in a semi-infinite medium, this force varies as $1/R$, when R , the distance from the surface, is large, and that it is equal to the force which would be exerted in an infinite medium between this dislocation and another of opposite sign situated at the image of the first dislocation in the surface. It is convenient to call the force which arises because of the presence of a surface an "image force". Of course, in this model the presence of other nearby surfaces means that differences between various image forces are observed. In crystals of normal size the dimensions are much larger than the strength of the dislocations, so that the image forces are often less important than other forces of interaction. In this model, however, the strength, λ_0 , of a dislocation is not many times smaller than the linear dimensions of the solid. The image forces are thus very strong, and it is necessary to make sure that they do not interfere with other effects which are being studied. This can generally be done by making the model symmetrical, so that opposing image forces balance. Dislocations are attracted to the surface when the surface is free from traction. The nature of the image force may be altered by changing the boundary conditions. For example, if rigid bonds are inserted in the surface layers, so that the surface displacements are fixed, the model shows that the dislocation is repelled from the surface.

It should be noted (Figs. 1, 3, 4) that the image force tends to move the dislocation in that direction which causes a decrease in the volume of material where the strain-energy density is high (and an increase in the volume where it is low).^{*} This is true of interaction forces in general when they are determined by elastic-energy changes of the solid.

(c) *Deduction of Force on a Dislocation in the Model.*

The force on a dislocation, and therefore the manner in which it would move if free to do so, can be deduced by either of the following methods:

- (1) A row of bonds may be removed so that the dislocation lies in a position intermediate between its original position and the

^{*} The author is indebted to Professor A. H. Cottrell for this remark.

position one lattice spacing away. It is then easy to see from the asymmetry which of these alternative positions is the more favourable for the dislocation.

(2) The asymmetry of the shear strain of the adjacent material on the two sides of the dislocation may be examined. The dislocation tends to move towards the side where the strain is greater.

The magnitude of the force can be estimated qualitatively from the magnitude of these asymmetries.

(d) *Effect of External Stresses.*

Imagine that external tractions in the direction of the arrows are applied to the symmetrical model of Fig. 2. Then an asymmetry in the shear strains on the two sides of the dislocation appears, since the shear strains due to the dislocation and the external tractions reinforce each other on the right of the dislocation and partially cancel on the left. By the second rule of Section III (c) this shows that a force to the right is exerted on the dislocation by the external forces. If the dislocation moves in the direction of this force, the model slips in the direction of the externally applied tractions; the source of energy gain in this example is the work done by the external forces.

Inversion of the model makes it clear that for a given applied stress the forces exerted on positive and negative dislocations are in opposite senses. Obviously with a uniform shear stress, the magnitude of the force on the dislocation due to this stress does not vary with position.

(e) *Effect of Solute Atoms.*

Fig. 6 (Plate XCIII) illustrates how the strain energy of a crystal containing a dislocation and foreign atoms can be reduced by the formation of an "atmosphere" of solute atoms round the dislocation (Cottrell ⁷). The bonds 4-5 immediately below the dislocation have been replaced by longer ones representing the presence in this region of foreign atoms which expand the lattice (for example, carbon in iron). The energy of the model is much lower when the long bonds are in this position than when they are elsewhere in some general position in the lattice. In Fig. 7 (Plate XCIII) bonds 2-5 have been removed so that the dislocation lies in an intermediate position between 4-5 and 5-6, and at the same time an extra lattice plane has been added on the right to preserve symmetry with respect to the surfaces. The asymmetry of bonds 1-5 and 2-5 shows that the dislocation is attracted to the "foreign atoms" (without the long bond 4-5 the bonds 1-5 and 2-5 would be symmetrical). The dislocation and "atmosphere" have been further

separated in the model shown in Fig. 8 (Plate XCIII) by moving the long bonds to 3-4; this preserves the symmetry of the dislocation with respect to the surfaces. The asymmetry of bonds 1-5 and 2-5, which determines whether position 4-5 or 5-6 has the lower energy, is now hardly noticeable in the model. The attractive force to the "atmosphere" is reduced. The force in the slip direction on the dislocation due to the "atmosphere", is thus zero in the model in Fig. 6, rises as the dislocation moves away and then falls again, becoming very small when the "atmosphere" and dislocation are widely separated, since the energy of the system is then nearly independent of their relative position. This has been made the basis of a theory of the sharp yield point of iron (Cottrell,⁷ Nabarro,⁸ Cottrell and Bilby⁹). The yielding process may be demonstrated by applying to the model in Fig. 7 an external shear just sufficient to counteract the asymmetry of bonds 1-5 and 2-5: on then moving the "atmosphere" as in the model of Fig. 8, a new asymmetry of these bonds appears showing that a net force acts on the dislocation away from the "atmosphere".

(f) *Forces between Dislocations.*

In Fig. 9 (Plate XCIV) the model is shown containing a positive and a negative dislocation on the same slip plane. This state is obtained by making the material above the slip plane between the dislocations slip one lattice spacing to the right with respect to that below, while the material outside the dislocations remains unslipped. The two dislocations form the boundaries between the slipped and unslipped material. In Fig. 10 (Plate XCIV), the dislocations are further separated and the slipped region extended. If each dislocation in Fig. 10 is moved two spacings away from the other, the slip spreads over the whole slip plane, and the dislocations pass out of the model, leaving a perfect lattice in their wake, with the upper half displaced one lattice spacing to the right with respect to the lower. If the dislocations in the model in Fig. 9 are each moved one spacing towards the other, mutual annihilation occurs (the slipped region shrinks to nothing) and an unslipped regular lattice results. To produce unit slip to the right of the upper half with respect to the lower thus requires either the passage of one dislocation across the whole slip plane (Section III (a)), or the passage of each dislocation of an unlike pair of the same strength across half the slip plane.

The force between the members of such a pair may be studied by examining the force on one dislocation as the other is moved relative to it, and it is convenient to balance this force against image forces. A series of models is made in which the positive dislocation remains in the

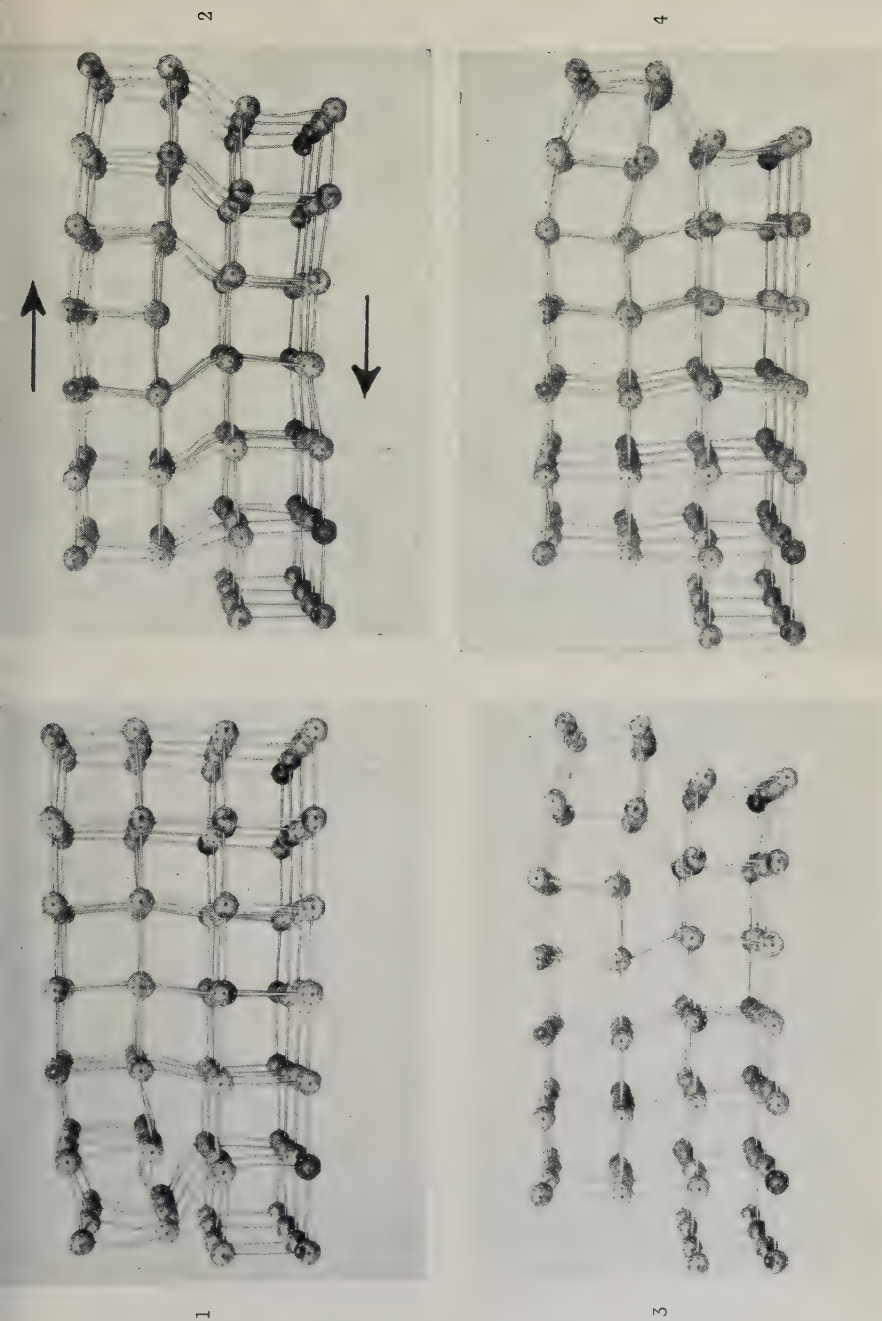
same position with respect to the boundary surfaces, so that the net image force on it is constant, while the negative dislocation moves relative to it. Changes in the force on the positive dislocation are then due to the motion of the other. In Fig. 5 the net image force on the single positive dislocation in the position intermediate between 1-2 and 2-3 acts to the right. A negative dislocation introduced in the model in Fig. 11 (Plate XCIV) reduces the asymmetry of bonds 2-4 and 2-5 and thus attracts the first dislocation. As the negative dislocation approaches the positive the force of attraction increases, until in Fig. 12 (Plate XCIV) it exceeds the net image force on the positive dislocation. Calculations show that the interaction force between two dislocations in an infinite medium varies inversely as their distance of separation; it is thus of the same type as the image force.

The interaction between the dislocation pair may be inferred from the models in Figs. 9 and 10. If either dislocation is removed, the other is clearly subject to a net image force. These image forces are equal on account of the symmetry, and act in opposite senses on the two dislocations, that on the positive being towards the right. However, the image forces are greater in the model of Fig. 10 because the dislocations are nearer the surfaces. In the model in Fig. 9 the material between the dislocations (where their strain fields are reinforcing each other) is more highly strained than that outside them; they would thus run together and annihilate each other if free to move. The force of attraction between them at this separation is stronger than the equal image forces on either. In the model of Fig. 10 the shear strain of the adjacent material on the two sides of each dislocation is about the same; the attractive force between the pair at this separation is roughly equal to the image force on either (the image forces have increased and the attractive force has decreased). Further separation means that the dislocations would separate if free to move, so that the model of Fig. 10 represents a position of unstable equilibrium. In a model large enough for the image forces to be negligible compared with the attractive force and to which a uniform external shear stress is applied, the above discussion shows that there will be a critical distance of separation at which the dislocations will be in unstable equilibrium. For equal forces, opposite in sense and independent of position, will act on the two dislocations due to the external stress, and they will separate only if they reach the critical separation at which the attractive force between them is just equal to the force on each due to the applied stress. There is thus an activation energy for the spread of slip by separation of a dislocation pair under a given shear stress.

IV.—SCREW DISLOCATIONS.

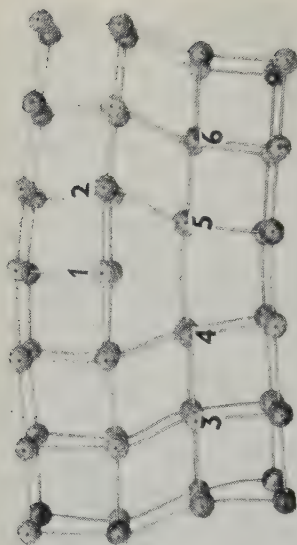
The line of the edge dislocation lies perpendicular to the direction of slip. J. M. Burgers¹⁰ has described another simple type in which the slip-vector (representing in direction and magnitude the strength of the dislocation) lies parallel to the dislocation line—the “screw” dislocation. Figs. 13–15 (Plate XCV) show the passage of such a dislocation across a model, causing unit slip to the left of the upper half with respect to the lower. The slip plane is roughly horizontal and passes through the middle of the model. The dislocation enters from the front in the model in Fig. 13; here the upper half of the nearest vertical lattice plane has slipped one lattice spacing to the left with respect to the lower, the rest of the model has not slipped, and the screw dislocation appears naturally as the boundary line, lying *parallel* to the slip direction, between the slipped and unslipped regions. It lies horizontally in the slip plane along the front row of lattice cells. A point which continuously circles the dislocation line, moving on the lattice planes (as defined by the bonds) pursues a spiral path. A series of balls nearest to the dislocation line on such a path have been numbered in order in Fig. 13: the third and seventh balls, which have not been numbered, can be seen behind 4 and 8, respectively. The reason for the name “screw” is thus obvious. This is a left-hand screw dislocation; a displacement of the front vertical plane of the model in the reverse direction (that is, to the right) would produce a right-hand screw, the resulting model being a mirror image of that in Fig. 13.

The slip spreads by the dislocation line moving in the slip plane into the model, away from the observer. In the model in Fig. 14 it has moved one spacing and lies along the central row of lattice cells; the front two planes have slipped and the rear two have not. This photograph shows clearly the helical surface formed by the lattice planes about the dislocation line, and also the elastic strains in the model. Round a screw dislocation in an infinite isotropic elastic medium no dilatation occurs (although, presumably, there must be some in a close-packed structure); the expected symmetrical shears appear in the model. On account of the finite size, the lattice planes are twisted. In the model in Fig. 15, the near three planes have slipped and the dislocation line is along the (middle) rear row of lattice cells. Further movement away from the observer causes the dislocation to pass out of the model leaving a perfect lattice in its wake, but with the upper half displaced to the left of the lower by one lattice spacing. Thus the passage of this screw dislocation across the model from the front to the rear produces the same slip as the passage of a positive edge dislocation of

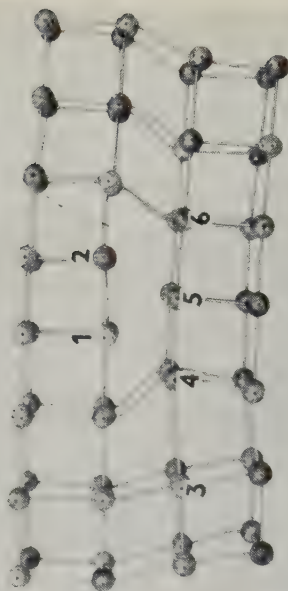


FIGS. 1-4.—Passage of a Positive Edge Dislocation from Left to Right Across a Simple Cubic Lattice.

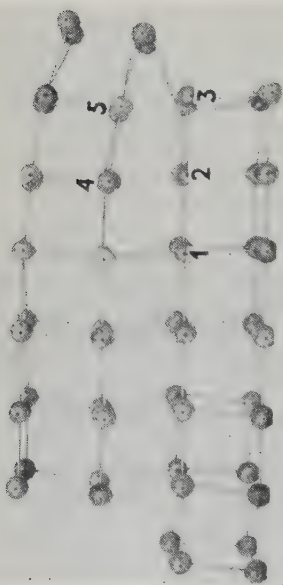
6



8



5



7

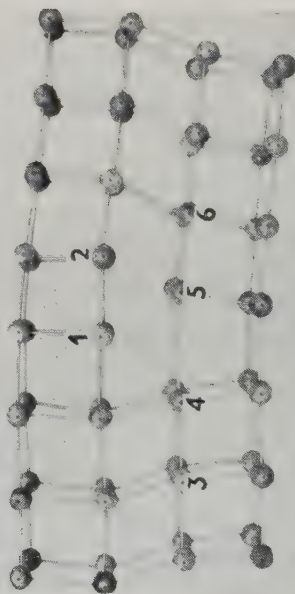
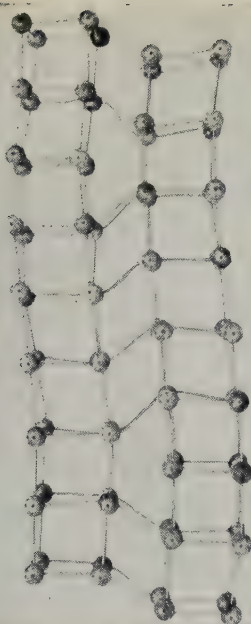
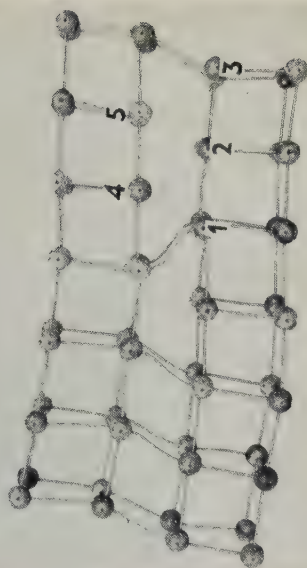


FIG. 5.—The "Image" Force of a Dislocation. FIGS. 6-8.—Interaction of an Edge Dislocation and an "Atmosphere" of Excitons. Atoms

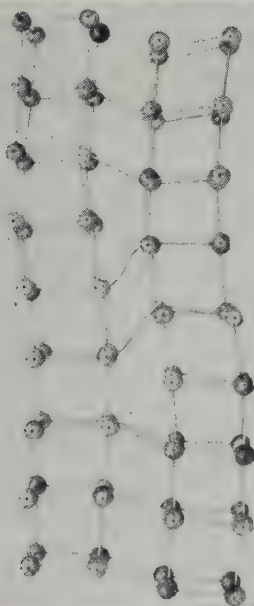
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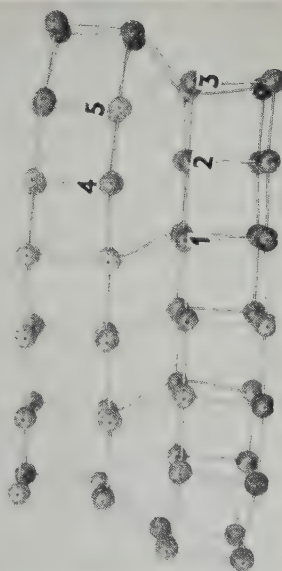
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9

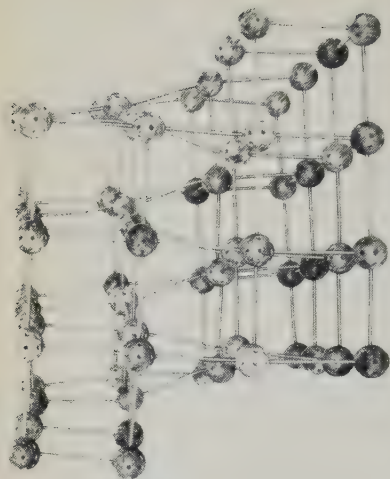


11

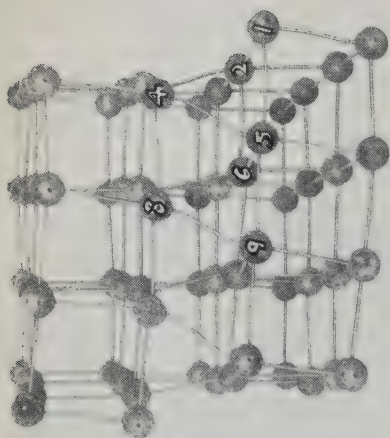


FIGS. 9 AND 10.—Two Unlike Edge Dislocations on the Same Slip Plane.
FIGS. 11 AND 12.—Interaction of Two Unlike Edge Dislocations on the Same Slip Plane.

14



13



15



FIGS. 13-15.—Passage of a Left-hand Screw Dislocation, Lying Horizontally and Parallel to the Plane of the Paper, Across a Model from the Front to the Rear.

17

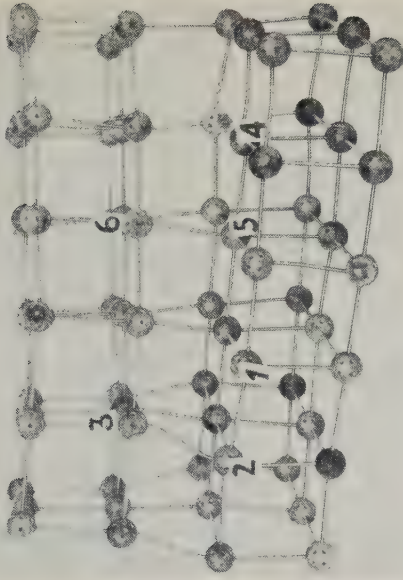


FIG. 17.—Two Parallel, Like Screw Dislocations.

16

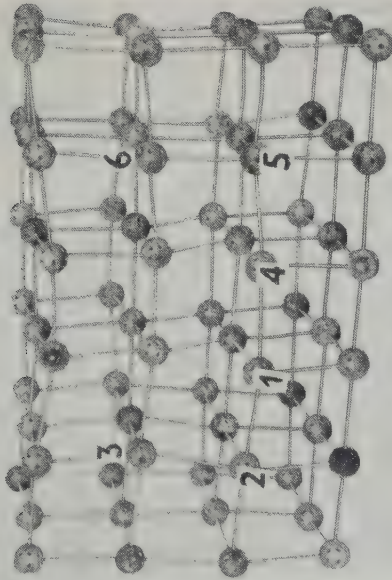
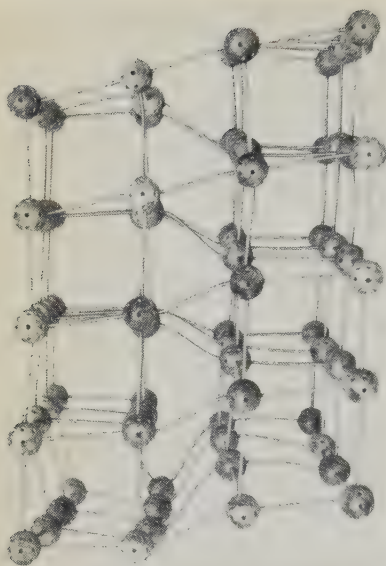
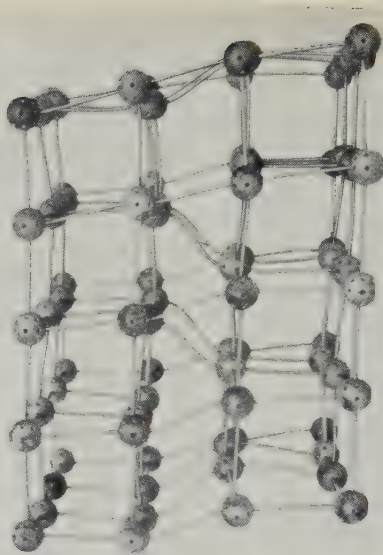


FIG. 16.—Two Parallel, Unlike Screw Dislocations.

19

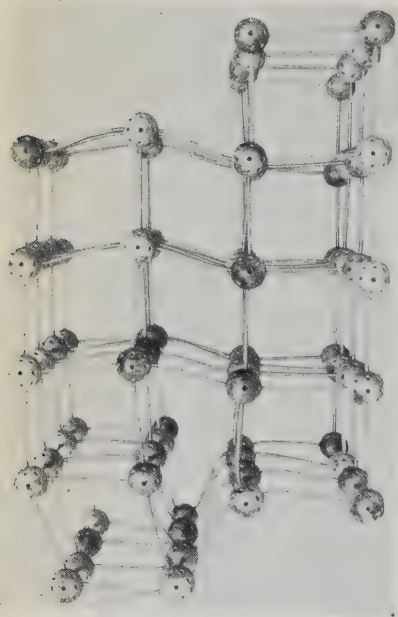


21



FIGS. 18-21.—Illustrating a Region of Local Slip.

18



20

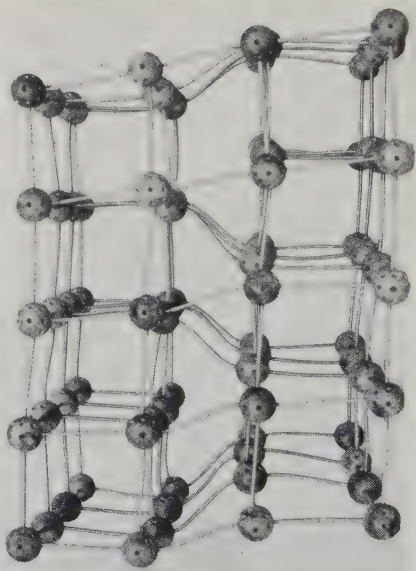
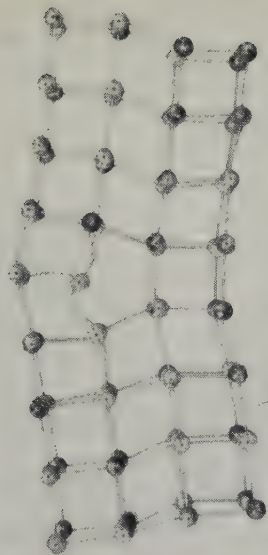


FIG. 18.—Only the Left-hand Surface Layer Unslipped. FIG. 19.—The Left-hand and Front Surfaces Unslipped. FIG. 20.—The Left-hand, Right-hand, and Front Surfaces Unslipped. FIG. 21.—All Surfaces Unslipped. (Note: The text is partially obscured and difficult to read in the original image.)

23

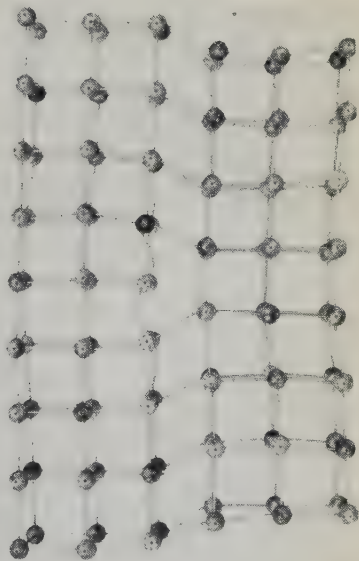


FIGS. 22-24.—A Positive Edge Dislocation in Models of Increasing Thickness Perpendicular to the Slip Plane.

22



24



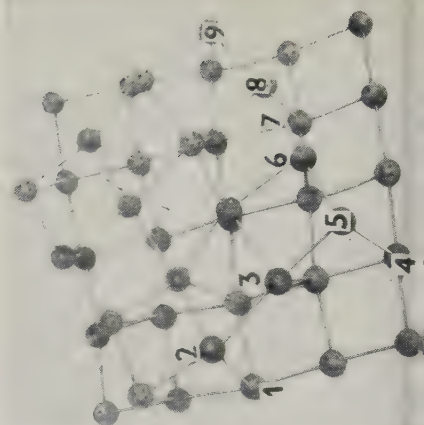
26



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28



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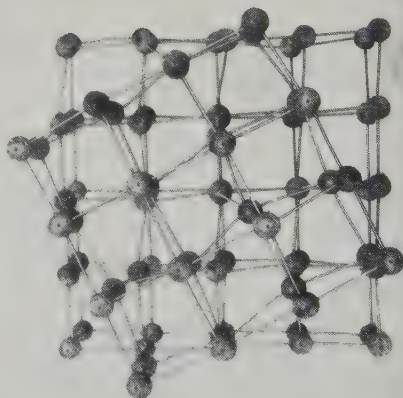


FIG. 25.—Array of Like Edge Dislocations Forming a Boundary Region between Lattices of Different Orientation.

FIG. 26.—Interaction of an Edge Dislocation with an Incomplete Array of Similar Dislocations.

FIG. 27.—Rotation of One Lattice Block with Respect to Another, caused by a Crossed Grid of Like Screw Dislocations between them.

FIG. 28.—Structure of a Transition Surface Consisting of a Crossed Grid of Like Screw Dislocations.

the same strength across the model from right to left. As slip spreads by the propagation of a screw dislocation steps appear on steadily increasing portions of the model surfaces; when it spreads by the propagation of an edge dislocation on the other hand, the step appears suddenly along the whole of one surface as the dislocation enters, and suddenly along the whole of the other surface as the dislocation leaves. This difference is important when the dynamic behaviour of dislocations is considered (Frank ¹¹).

Models of the passage of a right-hand screw dislocation across the model in Figs. 13-15 may be seen by holding the photographs up to a mirror. Motion of left-hand and right-hand screw dislocations in the same direction causes slip in opposite directions.

The screw dislocation in Figs. 13-15 is viewed in a direction at right angles to its line; screw dislocations viewed approximately along their line are shown in Fig. 16 (Plate XCVI), where the balls 1, 2, 3, and 4, 5, 6 mark respectively the beginning of right- and left-hand screw dislocations lying parallel to each other. This dislocation pair has been made in the model by causing the twelve central balls of the upper half to slip one lattice spacing with respect to the rest of the model, in a direction away from the observer, on a horizontal slip plane, the remainder of the model remaining unslipped. Mutual annihilation occurs if the dislocations each move one spacing towards one another, while if they each move two spacings away from one another a perfect structure results, with the upper half displaced in a direction away from the observer by one spacing with respect to the rest. In the model shown in Fig. 17 (Plate XCVI), the left-hand screw dislocation beginning 4, 5, 6 in Fig. 16 has been replaced by a right-hand screw dislocation also beginning 4, 5, 6. The model now contains two like parallel screw dislocations separated by two lattice spacings. This causes the upper half to be rotated with respect to the lower about an axis perpendicular to the slip plane, and at the same time the lattice planes are twisted. If these dislocations are moved together, a screw of double pitch appears: this requires severe distortion of the model.

By disconnecting lines of the lattice so that screw dislocations lie in intermediate positions, or by study of the differences in shear strain, interaction effects may be demonstrated. For example, the application of an external shear stress in the direction necessary to cause the slip shown in Figs. 13-15 introduces an asymmetry from which it may be deduced by the second rule of Section III (c) that a force is exerted on the dislocation in a direction away from the observer.

V.—COMBINATIONS OF EDGE AND SCREW DISLOCATION.

Like vortex lines in a fluid, dislocation lines in a crystal must either be closed in themselves or must extend to the outer boundaries. The model shown in Fig. 18 (Plate XCVII) contains a positive edge dislocation on the left. In Fig. 19 (Plate XCVII) the dislocation has been ended at the front surface of the model, by rejoining the bonds so that this *surface* is unslipped. This operation automatically generates a right-hand screw dislocation beginning at the near end of the edge dislocation and lying horizontally in the slip plane along the near row of lattice cells. The model now contains two dislocation lines at right angles which divide the unslipped surfaces on the left and in front from the rest of the model, where the upper half has slipped to the left with respect to the lower. The continuous helical surface formed about the screw dislocation by the lattice planes is terminated by its emerging as the extra "half-plane" of the edge dislocation.

If, in the model of Fig. 19, the edge dislocation moves, but the screw does not, it either annuls increasing lengths of the screw at its near end (motion to the right) or "trails" screw dislocation behind it. Similarly, if the screw dislocation is moved alone, the edge dislocation is either steadily diminished or steadily increased in length. Once the edge or screw dislocations are present in the model, their motion requires only small energy changes. Thus, given the presence of dislocations, some anchored and others in motion, more dislocations can be generated by a steady cumulative process, no step of which requires energy comparable with the self-energy of a long dislocation line.

The screw dislocation in the model in Fig. 19 may be terminated on the right by rejoining bonds so that the right-hand surface is also unslipped. Fig. 20 (Plate XCVII) shows that this operation automatically generates a negative edge dislocation parallel to the first edge dislocation, beginning from the end of the screw dislocation and extending to the back of the model. As before, the continuous helical surface round the screw dislocation ends on the extra plane of the edge dislocation. The model now contains a line of dislocation forming three sides of a square, consisting of a positive edge, a right-hand screw, and a negative edge, in that order. This line of dislocation separates the unslipped surfaces on the left, in front, and on the right, from the rest of the model, where slip has occurred.

A simple rule for deciding rapidly the types of screw and edge dislocation which meet at an internal point is as follows : "The clenched hand is imagined to be placed in the slip plane with the arm along the line of the edge dislocation and the *back* of the hand towards the extra

half-plane, so that the thumb points along the screw dislocation. The latter is a right-hand screw if the right hand must be used, and vice versa."

A point moving from the extra plane of the edge on to the helical surface about the screw, follows, of course, the line of the arm and fingers.

The edge dislocations shown in Fig. 20 may now both be ended at the rear of the model, by rejoining bonds so that the rear surface is unslipped. This automatically links the ends of the edge dislocations by a screw dislocation, which the rule given above shows to be left-handed. Fig. 21 (Plate XCVII) shows the model in this state. It now contains a closed dislocation line in the form of a square, consisting of a positive edge, right-hand screw, negative edge, and left-hand screw in that order. This forms the boundary between the four surfaces of the model which have not slipped, and the interior where slip of the upper half to the left with respect to the lower has occurred. Thus the model contains a region of local slip with the dislocation loop as its boundary, and can in fact be made by the one physical operation of causing slip to occur internally while the surfaces remain unslipped: this operation automatically generates the four dislocation lines that have been inserted one by one.

The signs of the shear strain of the material in the slipped and unslipped regions are different, but the magnitudes of the shear strains immediately adjacent to the two sides of any part of the dislocation loop depend, as with the models of Figs. 9 and 10, on the size (and shape) of the model. It is clear, however, that as more material is built on externally, so that the size of the loop becomes much smaller than the size of the model, the strain in the slipped region on the inside of the loop will become greater, and that on the outside will become less. Application of a sufficient shear stress in the direction which decreases the strain in the internal slipped region will cause the loop to spread, but discussion of the stability of the loop is complicated by the fact that the line of dislocation increases in length as the slip spreads. A loop in an infinite medium (where there are no surface forces and no periodic equilibrium positions for the dislocations due to a crystalline structure) will shrink to zero if the dislocations are free to move. Under an external stress there will be a critical loop size corresponding to an energy maximum; the presence of surfaces and a crystalline structure will modify the critical size for a given stress. A loop smaller than this critical size will shrink and one greater will expand. If all the dislocations in Fig. 21 are moved one lattice spacing towards the nearest surface, they pass out of the model and a perfect lattice results, but with the upper half

displaced one spacing to the left with respect to the lower. Thus unit slip of the upper half with respect to the lower may be produced by forming a region of local slip entirely within the model and causing this region to expand until it covers the entire slip plane.

VI.—ARRAYS OF DISLOCATIONS IN TRANSITION SURFACES.

Transitional regions in a crystalline structure between two domains of different orientation, such as grain or mosaic block boundaries, can be described by arrangements of screw and edge dislocations. With a suitable combination of these dislocations the transition from the one regular lattice to the other occurs abruptly, the irregular region being only a few lattice spacings across. The difference in orientation of the two domains depends on the strength of the dislocations and their arrangement in the transition surfaces. In general, the closer the packing of the dislocations in the transition surfaces, the larger the difference in orientation of the two domains. On account of the small size of the model it is necessary to pack dislocations closely, so that transitions through quite large angles are obtained; these angles may be reduced by increasing the spacing of the dislocation arrays.

No relative rotation of the two halves of the slip plane at large distances is caused by introducing an edge dislocation into an infinite crystal. But if the crystal is finite in a direction (initially) perpendicular to the slip plane, such a rotation does occur (Cottrell¹²). This effect is illustrated by a series of models each containing a positive edge dislocation. As the thickness of the models in the direction (initially) perpendicular to the slip plane increases, the rotation becomes less pronounced (Figs. 22–24, Plate XCVIII). The buckling of the bonds shows that there is an increase in the elastic energy stored locally near the dislocation as the size of the model increases; this is in accordance with the elastic theory for an edge dislocation in a finite solid with no tractions applied to the outer boundaries. In the models in Figs. 23 and 24, the surface layers above the dislocation are in tension, and those below it are in compression, although layers immediately above the dislocation are in compression and immediately below in tension. A series of models all identical with any of those shown can be joined together with little change of elastic energy to increase the thickness in the direction (initially) perpendicular to the slip planes. In this way an equally spaced periodic array of like edge dislocations is obtained, and the lattice on either side is rotated symmetrically about an axis lying in the slip planes. (The dislocation array really consists of two linear arrays in close proximity, since the numbers of balls on the upper and lower

surfaces are unequal). J. M. Burgers¹⁰ has treated a regular infinite array of this kind, and has shown that at large distances the lattice planes are inclined to each other at an angle 2α , where $\tan \alpha = \lambda_0/2h$, λ_0 being the slip distance and h the spacing of the dislocation array. Fig. 25 (Plate XCIX) shows an array in a finite model with a dislocation on every lattice plane ($\lambda_0 = h$); this may be made by running in edge dislocations from each block on alternate lattice planes. The model is very slightly distorted by its own weight; this causes the small shear strains remote from the transition surface. With this particular spacing of dislocations, the lattices of the two domains are almost perfect except in the immediate neighbourhood of the transition surface, so that the strain energy is very small when the domains meet at this angle. With transition surfaces made by assembling models identical with those in Figs. 23 or 24, for example, the strain is not so localized, and the strain energy of the model is larger.

The energy of an assembly of models of *different* thicknesses each containing an edge dislocation will be larger than an assembly of identical models because of the incompatibility of the blocks. Thus the density of any such array of dislocation lines will tend to become uniform if re-arrangement can occur. In particular, a non-uniform array may be expected to attract suitable dislocations to complete itself. To illustrate this a dislocation, previously over the bond 3-4 (Fig. 25), has been moved two lattice spacings away to lie over the bond 1-2 (Fig. 26, Plate XCIX). The asymmetry of the shear strains on the two sides of the dislocation in its new position shows that although it is now quite near to the outer surface (and hence subject to an image attraction from this surface) it is still attracted back to its position in the array. The existence of such an attractive force has been confirmed by calculations based on the elastic theory.¹³ The "polygonization" obtained by Cahn¹⁴ in zinc crystals has been explained by the process of assembly of dislocations in transition surfaces; this process and many of the concepts of W. G. Burgers,¹⁵ who has discussed recovery and recrystallization from the point of view of the dislocation theory, could be demonstrated in a larger model. Transition surfaces consisting of double sets of edge dislocations lying on slip planes at right angles (J. M. Burgers¹⁶) may also be made in the model.

Fig. 27 (Plate XCIX) shows a model with a transitional region between two lattice blocks which have suffered a relative rotation about an axis perpendicular to the transition surface. Such a region may be described by a crossed grid of like screw dislocations lying in the transition surface. A single set of parallel screws produces not only a rotation (see Fig. 17) but also a general shear; with the addition of the comple-

mentary set the strain extends only to distances of the order of h from the transition surface, where h is the spacing of the grid (Frank¹¹). In the model shown, the angle of rotation corresponds to a grid spacing of two lattice spacings and the screw dislocations are all right-handed. The structure of the transition surface may be seen in detail from Fig. 28 (Plate XCIX), where one plane only of each block is shown: these planes are distorted because there is no supporting lattice attached to them. The lines of the first set of screw dislocations lie parallel to a vertical direction [010] in the far plane. Two occur in the model and begin with the balls 4, 5, 6 and 7, 8, 9; no screw dislocation lies along the row of cells between them, for the cell whose lower surface contains the balls 6, 8, 7 is merely distorted. The lines of the complementary set lie parallel to a [100] type direction in the near plane, which was perpendicular to the lines of the first set before the relative rotation occurred, that is, a direction which was parallel to the [100] direction in the far plane before the rotation. One of these dislocations begins with the balls 1, 2, 3, and as the upper plane is only three cells square this is the only dislocation of this set present. To extend the model, screw dislocations must be inserted along every alternate row of lattice cells in each block, so that a uniformly spaced crossed grid is obtained. The easiest way to make such a model (Fig. 27) is to insert the sets of screw dislocations separately, one in each block, and run them together into the transition surface. The removal of strains from the neighbouring regions of the structure caused by the introduction of the complementary set is quite marked.

By combining arrays of screw and edge dislocations, more complicated models can be built. An interesting model is that of one crystal block completely enclosed by another and rotated with respect to it.

VII.—DISLOCATIONS IN OTHER LATTICES.

Body-centred and face-centred cubic lattices and hexagonal structures can be made with the model. Thus the half dislocation proposed by Heidenreich and Shockley¹⁷ and the sessile dislocation of Frank¹⁸ can be demonstrated. The detailed discussion of the forms of dislocations in these more complicated lattices has yet to be carried out, and it is hoped that the model will prove useful in this work.

VIII.—CONCLUSION.

The model described in this paper does not, of course, provide evidence that slipping occurs in crystals by the propagation of dislocations. It is of assistance, however, in studying the geometrical effects of the

motion of dislocations of various types and of their assembly in arrays, particularly in the more complicated lattices. It also illustrates simply in a qualitative way many results of the elastic theory. As a model of crystal structure it suffers from the same limitations as those made with wooden balls and rigid rods. The use of some simple bond which would readily undergo extension and compression along its length (for example, a thicker spring, more openly spaced) would be an improvement.

ACKNOWLEDGEMENTS.

The author is indebted to Professor D. Hanson for his advice and encouragement, and to many colleagues in the Department, particularly Professor A. H. Cottrell and Mr. F. R. N. Nabarro, for valuable discussions. He wishes to thank Dr. T. Ko for his advice and collaboration in the photography.

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← Direction of Applied Stress.



FIG. 1.—Aluminium Specimen electropolished in orthophosphoric acid, after tensile test at 20° C. $\times 100$.



FIG. 2.—Aluminium Specimen prepared and deformed in identical manner to the one shown in Fig. 1, but chemically etched before deformation. $\times 100$.

NOTE ON THE USE OF ELECTROPOLISHING 1236 IN THE METALLOGRAPHIC STUDY OF PLASTIC DEFORMATION.*

By G. R. WILMS,† B.Met.E., M.Eng.Sc.

SYNOPSIS.

Attention is drawn to some misleading observations that may be made if the anodic films are not removed from electrolytically polished specimens used for the metallographic study of plastic deformation.

IN view of the increasing use of electropolishing for preparing surfaces suitable for the study of plastic deformation, it is thought of interest to record the following observation, which shows that care is necessary if certain spurious effects are to be avoided.

An unusual effect was observed during a recent investigation on the plastic deformation of specimens of super-purity aluminium electropolished in a solution of orthophosphoric acid of the following composition :

Orthophosphoric acid (90%)	.	.	40%
Ethyl alcohol	.	.	50%
Glycerine	.	.	10%

Satisfactory polished surfaces were obtained, accompanied by a light etching of the grain boundaries. The specimens were then submitted to tensile tests at room temperature (20° C.).

In the course of the tensile test, faint surface striations (slip) were first observed on the surface of the individual grains. However, on further deformation, when the applied nominal stress was of the order of 2000 lb./in.², new deformation markings suddenly appeared in the form of continuous, widely spaced, dark lines spreading over the grains at right angles to the direction of applied stress, and extending across the grain boundaries. With progressive deformation these lines became broader, and a cellular pattern of lines developed within the continuous lines, as illustrated in Fig. 1 (Plate C), which was obtained after final fracture of the specimen. It will be noted that there is no obvious evidence of the normal well-known slip lines.

These surface markings may be attributed to the cracking of a thick

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anodic film which is formed on the specimen during the electropolishing process and which is not removed by subsequent washing in water. It is to be expected that such a film will crack with progressive deformation in the manner already described, and also that it will obliterate any evidence of slip on the underlying metal. The true changes in the metal are thus masked.

To demonstrate this, the anodic film was removed by etching in the usual micro-etchant for pure aluminium, namely :

Hydrofluoric acid	2%
Nitric acid	25%
Water	73%

With the temperature of the etchant at 30° C., removal of the film, as determined by the onset of evolution of gas bubbles, required about 30 sec.

Fig. 2 (Plate C) shows a specimen prepared and stretched to fracture in exactly the same manner as for the one previously described, but in this instance the anodic film was removed by chemical etching before deformation. It will be clear that the metallographic appearance is now quite different, and shows the true changes.

Specimens polished in Jacquet's solution of perchloric acid-acetic anhydride did not show any such evidence of a thick anodic film.

Since many metals and alloys can now be conveniently electropolished, and a wide variety of electrolytes is being continually developed, it is hoped that this brief account will illustrate the necessity for removing the thick anodic film which may often persist after electropolishing even though the specimen is well washed.

THE STRUCTURE OF EUTECTICS.*

1237

By E. C. ELLWOOD,† Ph.D., A.I.M., MEMBER, and K. Q. BAGLEY,‡ B.Sc.

SYNOPSIS.

An investigation has been carried out into the crystal structure of four binary alloys, silver-copper, aluminium-copper, silver-aluminium, and iron-cementite, each of which consists at room temperature of a two-phase system in which the phases have been formed simultaneously at a higher temperature. In the case of the eutectic systems it was confirmed that orientation relationships exist between the two phases concerned, and these relationships were determined. It was found that a single crystal of eutectic acts, with logical exceptions, as a combination of two interlacing single crystals—one from each phase—and that the phases are aligned in such a manner as to cause least interference at the crystal interface. Relations were also observed between the direction of the temperature gradient—assumed to be the growth direction—and the crystallographic directions in the eutectic phases.

The possible effect of crystal structure and similarity of atomic spacing on solid solubility is briefly discussed.

I.—INTRODUCTION.

THE widespread occurrence of definite orientation relationships between crystals formed by recrystallization or precipitation suggests strongly that most, if not all, crystals formed in crystalline matrices inherit their orientations from the matrix crystals. As a further step it was desired to establish a connection between phases appearing simultaneously. Such a relation would directly control the formation of a eutectic, and to a lesser extent that of a eutectoid, since in the latter case the forces exerted by the matrix might be significant. Were such a relation to exist, it would result in the development of eutectic crystals possessing a quasi-uniform structure, similar in their overall lattice regularity to a single crystal, but comprising two individual lattices interpenetrating on a macroscopic scale. The existence of the relation and the form it assumes in any particular eutectic should therefore be capable of demonstration by X-ray means.

The metal systems chosen for examination involved relationships, respectively, between two cubic phases, a cubic and a tetragonal phase, and a cubic and a hexagonal phase. The eutectic series was obtained by combination of silver and copper to produce the silver-copper eutectic, which is formed between the saturated solid solutions of each

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metal in the other, both phases being cubic; of aluminium and copper to produce the eutectic between the aluminium-rich solid solution of copper in aluminium and the intermetallic compound, θ , the phases being cubic and tetragonal, respectively; of aluminium and silver to produce the eutectic between the cubic aluminium-rich solid solution of silver in aluminium and the hexagonal solid solution, γ , the composition of which approximates to the formula Ag_3Al_2 .

Later, when eutectoids were included in the investigation, pearlite was chosen in preference to simpler systems, and in the face of anticipated difficulties, because it is by far the most common and important example of this type of structure. In pearlite body-centred cubic ferrite is in equilibrium with orthorhombic cementite.

While the study described in the present paper was proceeding references were found to similar investigations carried out by Straumanis and Brakšs^{1,2} who used the rotating-crystal method of X-ray analysis to demonstrate orientation relations in systems involving a hexagonal metal.

II.—GENERAL EXPERIMENTAL METHODS.

1. *Preparation of Alloys.*

The aluminium was kindly supplied by The British Aluminium Co., Ltd., and had the following analysis: silicon 0.0005, iron 0.0005, copper 0.0005, and aluminium (by difference) 99.9985%. The silver was of assay grade and the copper was electrolytically refined.

About 50 g. of each alloy was made up at a time. The composition was taken in the first instance from published data on the alloy concerned, but since the eutectic composition appears to depend upon the cooling rate, corrections were generally required to obtain samples free from primary crystals under the conditions of solidification employed in the production of X-ray specimens. The pure metals were melted together in alumina crucibles, and precautions were taken to prevent oxidation and to render the melt homogeneous. It was found that gas evolution during solidification under controlled conditions was troublesome, and in order to remove as much gas as possible the alloys were allowed to solidify slowly and then reheated to just above their melting points before the final samples were taken.

2. *Methods of Obtaining "Single Crystals".*

(a) *Solidification of Thick Rods under Controlled Conditions.*

Bars of 0.2 in. dia. and 2–3 in. in length were produced by casting metal into heated carbon moulds. These moulds were stoppered by the

insertion of carbon plugs and, thus sealed, were placed in an electric tube furnace for heat-treatment of the metal. Use was made of the temperature gradient found at the ends of such furnaces to induce nucleation of the melt at the cool end, followed by a slow advance of the solid-liquid boundary along the bar as the furnace cooled. This method could be relied upon to produce large-dia. eutectic colonies, very suitable for micro-examination, but was less desirable in the preparation of X-ray specimens because the bars were too thick for transmission work and thin sections had to be cut from them at the risk of cold working the material.

(b) *Slow Cooling of Thin Bars or Wires under Controlled Conditions.*

The thin bars were prepared either by drawing liquid metal up tubes of silica or hard glass, or, in the case of the silver-copper eutectic, by cold drawing 0.02-in.-dia. wires from small-dia. billets of the eutectic alloy. The wires produced were in both cases treated in a vertical gradient furnace, protected by small-bore silica tubing. The metal could be made to pass through the melting temperature at any rate of cooling between 10° and 300° C./hr. and, when the problem of obtaining an alloy crystallizing only as eutectic at a given cooling rate had been solved, the method produced specimens ideal for X-ray examination.

(3) *X-Ray Examination.*

Of the two principal means of determining the symmetry of single crystals, the rotating crystal and Laue methods, the Laue technique was adopted. The Laue patterns and data for each phase in the eutectic may be obtained by individual examination. Thereafter a similar examination of the duplex grain reveals the patterns of the two in conjunction, and these may be resolved and identified after gnomonic projection. From the projection, the alignment of the elementary cells, one with another, may be deduced. This information, combined with a knowledge of the crystal setting, allows conclusions to be drawn concerning the manner of growth with respect to the direction of the temperature gradient.

A tungsten target was used, at peak voltage 50 kV.

III.—THE SILVER-COPPER EUTECTIC.

The essential information concerning the silver-copper eutectic is given by Stockdale.³ Both metals are cubic, the lattice parameter of silver being 4.077 kX. units, and that of copper 3.608 kX. units; the

size-factor is therefore just within the limits of the Hume-Rothery rule for the formation of extended ranges of solid solution on both sides.

Specimens were obtained by passing material in thin silica tubes through the gradient furnace in such a manner that the cooling rate was 25°C./hr. at the eutectic temperature. Additional samples were obtained by cooling in the gradient at the end of a tube furnace. A flat was ground parallel to the axis of the bar so treated, and the surface was polished and etched in FeCl_3 solution to reveal the grain structure. Large eutectic colonies were picked out and thin sections taken from the surface on which they were found. These sections were mounted in transparent plastic and the irregularities on their surface due to cutting were removed. Thus the correspondence in appearance of the two sides of the metal strip could be confirmed.

Microscopic Examination.

The microstructure of typical sections of slowly-cooled samples is shown in Fig. 1 (Plate CI), in which rods of the copper-rich solid solution are shown dispersed in the silver-rich solid solution. Colony boundaries can be seen outlined by coarser copper particles. In the thicker samples crystals at the ends of the specimens were elongated in the direction of the gradient, but the general arrangement of the constituents remained unaltered. In the thinner wires, when free from excess of either constituent, the structure also showed response to the temperature gradient.

X-Ray Examination.

The X-ray examination was carried out mainly on thin sections of alloy prepared from 0.2-in. bars, as described, which for the purposes desired gave better transmission photographs than did the wires. They suffered to some extent from the effects of cold work induced by cutting the sections and from the longer exposure time necessitated by the increase in the obliquity with which the X-ray beam met the surface. Thus, the angles from which a particular specimen could be effectively photographed were restricted. The films obtained showed some asterism, but one characteristic feature soon became apparent, namely, that one pattern only was present. This extremely important characteristic persisted throughout and could not be attributed to the faintness of one constituent pattern, since diffraction images due to both were easily distinguishable on a powder photograph.

A Laue photograph yields a number of spots, each capable of being considered as a reflection from some particular set of crystal planes. Since the inclination of possible atomic planes is governed solely by

symmetry, the distribution of spots upon the photographic plate will depend only upon the symmetry of the crystal and its orientation with respect to the X-ray beam. Thus all cubic crystals with X-rays travelling along a particular axis give Laue spots at precisely the same positions. This would be equally true for any two similarly-oriented lattices with identical axial ratios and angles, the difference in atomic spacing in the two crystals being compensated by a change in the wavelength of the radiation reflected. Therefore the fact that a single pattern is obtained when a system containing two lattices is photographed, demonstrates conclusively that copper and silver, both face-centred cubic in structure, are oriented in such a manner that all planes and all directions in these planes are parallel. For only thus could the two patterns be coincident.

Asterism was obtained even in patterns from thin wire specimens obtained by carefully controlled cooling in the gradient furnace and also from annealed sections cut from the thicker bars. It is thought that this may be explained by the differential contraction of the two phases from the solidification or annealing temperature. It was also found that, when a relatively wide X-ray beam was used, single Laue spots tended to split up into two or three discrete spots, as though two or three crystals of slightly different orientation were contributing to the pattern. This is interpreted as indicating that in any colony of rods the orientation relationship of the two phases is perfect, but that individual colonies, while probably belonging to the same system of growth, suffer slight changes in orientation. Such slight variations in orientation in a single columnar crystal have been shown to exist by Northcott.⁴

IV.—THE ALUMINIUM-COPPER EUTECTIC.

Information about the constitution of alloys in the aluminium-copper system was taken from the diagram of Raynor.⁵ The θ phase is an intermetallic compound with a composition fairly close to CuAl_2 , in which aluminium has a small solubility, and which crystallizes in the body-centred tetragonal system. The dimensions of the unit cell are : $a = 6.052$ kX. units, $c = 4.878$ kX. units, axial ratio $c/a = 0.82$. Aluminium has a face-centred cubic structure with a lattice spacing of 4.041 kX.

The eutectic alloy was made up and allowed to solidify to expel dissolved gas, and then remelted. The liquid metal was drawn up heated tubes of silica or hard glass, forming wires of 0.5 mm. dia. and 5 cm. in length. These wires were passed through the gradient furnace from a maximum of 700°C. , at a rate of 60°C./hr. in the freezing zone.

The structure of the wires proved to be very sensitive to the rate of cooling in the gradient furnace and specimens free from primary constituent at moderate rates of cooling developed conspicuous primary dendrites of θ when an attempt was made to obtain a coarser structure by slower cooling. It was therefore necessary to correct the composition by adding a series of small quantities of the deficient element, so determining the correct composition by trial and error.

Microscopic Examination.

Chill-cast specimens in the unetched condition showed colonies of lamellar eutectic separated by areas in which the constituents were comparatively coarse. No grain boundaries proper could be distinguished, but etching for 5 sec. in 3% HF solution brought out a definite major structure, differentiating groups of the minor grains. The surface was apparently attacked after the manner of pure metals, and showed varying light and dark areas under the microscope. Each of the large grains included in itself numerous unit grains, and its boundary followed the coarser eutectic structure.

The slowly-cooled specimens showed structures on a larger scale, and of greater variety, as illustrated in Fig. 2 (Plate CI). The dark-etching continuous phase is θ and the light, disperse phase is the aluminium solid solution. The etching reagent was 10% HNO_3 in water. The direction of the lamellæ was apparently strongly influenced by the direction of the temperature gradient, the long axis of the lamellæ tending to be aligned perpendicular to the solidification front.

X-Ray Examination.

The X-ray examination was carried out on wires cooled in the gradient furnace. From these wires, well-defined single spots were quickly obtained. The first patterns were exceedingly complicated and the number of spots suggested the presence of more than one pattern. By manipulation of the crystal, in a manner dictated by previous photographs, views were obtained along a four-fold axis of symmetry of the aluminium phase which was found to coincide with the four-fold axis of the θ phase, and along a four-fold axis of the aluminium phase, at 90° to this, which showed two-fold symmetry in the θ phase. Projection of the Laue photographs so obtained confirmed the accuracy of the setting and analysis proved the phases to be oriented in such a manner that all faces and all edges of the tetragonal prism were parallel to all faces and edges of the aluminium elementary cube. The X-ray patterns showed that the (001) axis of the θ phase was perpendicular to

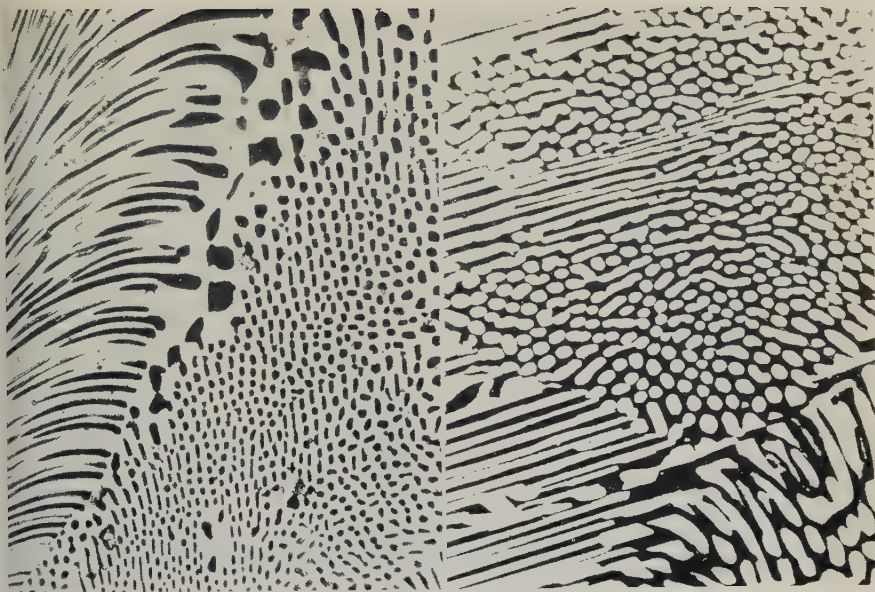


FIG. 1.—Silver-Copper Eutectic. $\times 200$.

FIG. 3.—Silver-Aluminium Eutectic. $\times 200$.

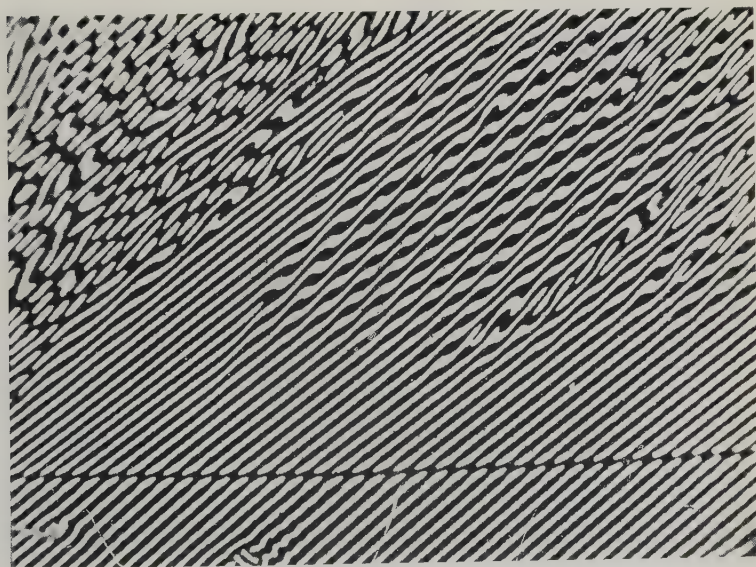


FIG. 2.—Aluminium-Copper Eutectic. $\times 250$.

[To face p. 636.]

the length of the specimens. Thus, it may be inferred that the θ phase grows with its (001) axis perpendicular to the temperature gradient. The axial ratio of the tetragonal prism was found to be 0.81, in good agreement with the accepted value.

V.—THE SILVER-ALUMINIUM EUTECTIC.

Most of the information regarding the silver-aluminium system was taken from Hansen's ⁶ equilibrium diagram. Westgren and Bradley ⁷ describe the γ phase as a simple solid solution in which aluminium and silver atoms are distributed in a random manner on the points of a close-packed hexagonal lattice. The phase is homogeneous in the range from 27–40 at.-% aluminium and has lattice dimensions changing continuously from $a = 2.865$ kX. units, $c = 4.653$ kX. units, and $c/a = 1.625$, when saturated with silver, to $a = 2.879$ kX., $c = 4.573$ kX., and $c/a = 1.588$, when saturated with aluminium. Aluminium itself has a face-centred cubic structure of side 4.041 kX. Since silver has a lattice parameter of 4.077 kX. the extensive solid solubility can be easily understood.

Microscopic Examination.

The wires used as X-ray specimens and a slowly cooled bar were examined on a longitudinal section. A suitable etching reagent was very dilute FeCl_3 solution or, better still, 2% HF solution. Examples of typical structures are shown in Fig. 3 (Plate CI).

The grains were large and grain boundaries usually distinct, the discontinuous phase appearing to separate here in considerable quantities. The aluminium forms the continuous matrix, the γ phase appearing as rods, lamellæ, or the intermediate structure seen in Fig. 3. Compositions giving eutectic only in chill-cast specimens required correction before the constituent in excess was eliminated from wires treated in the gradient furnace. An alloy containing 29.5% aluminium and 70.5% silver gave a satisfactory structure under the cooling conditions employed.

X-Ray Examination.

This was carried out on wires only. A vertical wire showed in the beam a comparatively simple pattern symmetrical about a horizontal line. A four-fold axis was found by merely rotating the crystal about the vertical axis. Evidently aluminium, the continuous phase, exercises directive power and grows as usual with the (001) fibre axis parallel to the direction of the temperature gradient. Tilting the crystal to bring a (111) plane perpendicular to the X-ray beam produced a pattern

of multiple symmetry in which three-fold symmetry was clear and six-fold symmetry probable. Projection showed that the base of the hexagonal prism grew parallel to a (111) plane of aluminium. The presence of faint extraneous spots and the fact that similar patterns were obtained, no matter which (111) plane was viewed, indicates that all four sets of (111) planes may be occupied by basal planes of γ hexagonal cells in a given crystal of eutectic. Hence the orientation relation between the planes may be stated definitely as :

$$(111)Al \parallel (0001)\gamma$$

Both phases may be visualized as a hexagonal arrangement of atoms, and it is found that the orientation of the close-packed lines in each case is identical, i.e. :

$$[110]Al \parallel [11\bar{2}0]\gamma$$

VI.—PEARLITE.

Some time was spent in an attempt to determine the orientation relation between ferrite and cementite in pearlite, but the difficulty in preparing specimens of pearlite suitable for X-ray examination prevented completion of the investigation. It is felt, however, that relations similar to those found in eutectics must also be found in eutectoids, and could probably be distinguished in systems less complex than the iron-iron carbide series.

VII.—DISCUSSION.

It has been shown, in the case of each of the three eutectics examined, that a simple orientation relationship exists between the two phases involved and that, as a first approximation, a single crystal of the eutectic may be considered as made up of interlacing single crystals of the two phases. While this simple picture is probably correct for the silver-copper eutectic, it may need some modification in the case of the more complex relationships that exist in the silver-aluminium eutectic. Here the basal planes of the hexagonal γ phase lie on the (111) planes of the aluminium-rich solid solution, but while there is only one set of basal planes in γ , there are four possible sets of (111) planes in the solid solution about which the γ can form. Evidence was indeed obtained that more than one set of (111) planes was involved. Similar considerations apply to the aluminium-copper eutectic, but in this case the non-cubic phase, θ , is continuous and therefore can have only one orientation in a single colony.

The relationships found are given in Table I.

TABLE I.—*Orientation Relationships in Eutectics of Binary Alloys.*

System.	Phases Formed.	Relationships.
Silver-copper.	Two f.c.c. phases.	All planes and directions parallel.
Aluminium-copper.	Al (f.c.c.), θ (b.c. tetragonal).	$(001)_{Al} \parallel (001)_{\theta}$ $[100]_{Al} \parallel [100]_{\theta}$
Silver-aluminium.	Al (f.c.c.), γ (c.p. hexagonal).	$(111)_{Al} \parallel (0001)_{\gamma}$ $[110]_{Al} \parallel [11\bar{2}0]_{\gamma}$
Pearlite (iron-cementite).	Fe (b.c.c.), Fe_3C (orthorhombic).	None found.

It is of interest to compare the relationships found with those obtained by other workers when the phases co-exist as a result of precipitation in the solid.

Barrett, Kaiser, and Mehl⁸ have shown that silver is precipitated on the (100) planes of copper with all planes and directions parallel to those of the matrix, which is exactly the same result as has been obtained in the present case when the two phases are formed simultaneously from the liquid.

In the case of the aluminium-copper system, an orientation relation between the aluminium-rich solid solution and precipitated θ has been obtained by Mehl, Barrett, and Rhines.⁹ The relation between the planes agrees with that obtained in the present investigation, but the alignment of directions, admitted to be questionable, is given as $[120]_{Al} \parallel [011]_{\theta}$, in place of the simpler relationship described above.

In the silver-aluminium system the orientation relationship for the phases produced from the liquid state agrees with that obtained when one phase is precipitated from the saturated solid solution. The relation is given by Mehl and Barrett¹⁰ as :

$$(111)_{Al} \parallel (0001)_{\gamma} \text{ and } [110]_{Al} \parallel [11\bar{2}0]_{\gamma},$$

which is in agreement with the present results.

An approximate measure of the degree of fit at the interface of any two phases may be obtained from figures of the lattice spacing of the appropriate phases. In the case of the silver-copper eutectic, the lattice spacing at room temperature of the silver- and copper-rich solid solutions are approximately 4.028 and 3.644 kX. units, respectively, so that about 10 unit cells of the copper-rich solid solution match 9 unit cells of the silver-rich solid solution quite accurately. Such figures must of necessity be rather rough until accurate lattice-spacing measurements of each phase are made at the eutectic temperature.

In the case of the aluminium-copper eutectic, it is found that the (100) planes of aluminium-rich solid solution, with lattice spacing of

4.041 kX., are formed on the (100) planes of θ , with lattice spacing 6.052 kX., so that three unit cells of aluminium fit quite well over two unit cells of θ .

The interatomic spacing on the (111) planes of aluminium is $\left(4.041 \times \frac{\sqrt{2}}{2}\right) = 2.857$ kX., while on the basal plane of the hexagonal γ phase in the silver-aluminium eutectic it is 2.817 kX. Here the degree of misfit is less than 2% at room temperature.

In a solid eutectic alloy, such as that of the silver-copper system, two solid solutions are in equilibrium, but it is of relatively little importance in the following discussion that they are present as a typical eutectic structure rather than as a primary solid solution with a secondary precipitate. Considering equilibrium between the phases, whether formed simultaneously or by subsequent precipitation from a solid solution, it would seem that the two main factors concerned are the chemical factor F_m and the surface-energy factor F_s . The magnitude and effect of the two factors separately is not known, but it could be postulated that where the surface-energy factor is small, i.e. in those cases where a high degree of fit is obtained between the two phases, it might be more economical to form a second phase rather than to increase the distortion of the parent lattice further by taking more material into solid solution. It is, in fact, suggested that considerations such as these may be of importance in determining the extent of the solid solution range, where the difference in atomic diameter is on the borderline of Hume-Rothery's 14% rule.

In the general case, the extent of solid-solution formation must inevitably depend upon the surface energy of the system. If an alloy which is in equilibrium under a given set of conditions is treated in such a way as to disturb the equilibrium, the change in free energy may be represented by :

$$\Delta F = -\Delta F_m + \Delta F_s,$$

neglecting the strain-energy term, and where ΔF_m and ΔF_s represent the changes in chemical and surface energy, respectively.

If conditions are altered without change in the free energy of the alloy, i.e. $\Delta F = 0$, then if ΔF_s is increased, say by a change in the size of the constituent parts, ΔF_m must also be increased if equilibrium is to be maintained. This can only occur by a decrease in the amount of material held in solid solution in one or both phases. It may thus be inferred that as the particle-size of one constituent of an alloy decreases, with a corresponding increase in area of contact between the two constituents, the amount of material in solid solution will decrease, and vice versa.

Such an idea is contrary to the accepted tenets of equilibrium in metallic systems, but receives some support from the work of Phillips and Brick,¹¹ who showed that the limits of solid solubility of copper in aluminium are dependent on the grain-size of the alloys. It is proposed to put the hypothesis to experimental test when an opportunity occurs.

It is often noted that lamellæ and rods of eutectic are curved, and this may be raised as an objection to arguments put forward in the present work. To meet this point, Fig. 4 shows diagrammatically the possible form of a curved boundary.

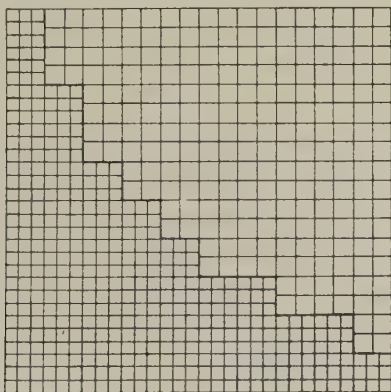


FIG. 4.—Alignment of Phases at a Curved Boundary.

Reference has been made to the direction of growth of the eutectic colonies during slow solidification. It has been assumed that the continuous phase is the one dictating the direction of growth, and the following relations have been found :

Silver-copper : Indefinite. Growth along (001) axis probable.

Aluminium-copper : (001) axis of θ perpendicular to temperature gradient.

Silver-aluminium : (001) axis of aluminium parallel to temperature gradient.

ACKNOWLEDGEMENTS.

The authors wish to express their thanks to their colleagues for helpful discussions while the work was in progress, and particularly to Professor C. E. Pearson for his encouragement of the research.

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REPORT OF COUNCIL

for the Year Ended 31 December 1949.

IN the opinion of the Council, the year 1949 has been one of the most successful in the Institute's history.

The outstanding event of the year was undoubtedly the Autumn Meeting in Paris. This meeting, which was held by invitation of the Société Française de Métallurgie and the French Non-Ferrous Metal Industries, was attended by a large number of members and ladies, and was a great success both from the scientific and technical and the social points of view. The Paris meeting has been the means of bringing together much more closely French and British metallurgists in particular, and the Council desires to express to the Institute's hosts the sincere thanks of the members not only for their invitation but also for the arrangements made for them and for the most generous hospitality offered.

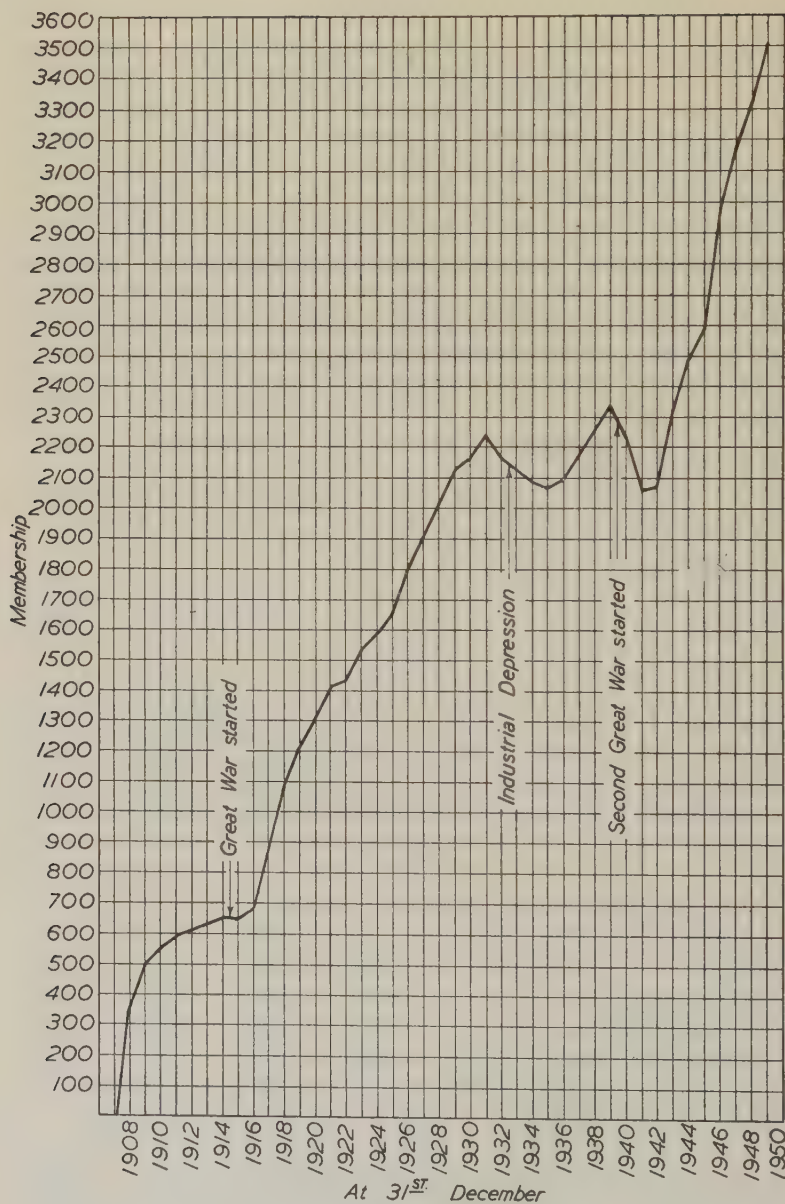
During the year two very successful and well-attended symposia have been held on "Metallurgical Aspects of Non-Ferrous Metal Melting and Casting of Ingots for Working" and "Metallurgical Applications of the Electron Microscope", respectively. A further symposium on "Metallurgical Aspects of the Hot-Working of Non-Ferrous Metals and Alloys" is being organized to be held in connection with the 1950 Annual General Meeting.

The first Students' Tour since the war, held in Birmingham during the 1949 Easter Vacation, was attended by nearly 100 Student Members. Reports indicate that such tours meet a real need, and the Council proposes to continue and to extend this service to Student Members.

The Council realizes that, to the majority of members, the receipt of the Institute's publications constitutes the main benefit of membership, and has endeavoured to strengthen this side of the work. In 1949 more papers have been published in the *Journal* than ever before, the standard of the matter published has been well maintained, and the subjects covered have been of wider interest to the members in general. The following figures show the increases that have taken place in the matter published in the *Journal* in the financial years (July-June) indicated:

	1945-46	1946-47	1947-48	1948-49
Number of papers, lectures, &c. .	33	40	31	52
Papers and discussions, pp. .	763	978	801	1143
Plates	49	82	59	115
Line figures	258	172	236	331
Half-tone figures	151	273	199	345
Metallurgical Abstracts, pp. .	460	520	720	824
Indexes, pp.	120	139	149	162
News and Programmes Section, pp.	77	170	216	198
Advertisement Section, pp. .	247	310	298	322

The considerable expansion of the *Journal* during the past few years is now considered not to reflect merely a post-war accumulation of work awaiting publication but to represent a state of affairs that will continue as a result of intensification of research in national, university, co-operative and commercial laboratories.



Curve of Active Membership of the Institute at 31 December 1908-1949.

So far as *Metallurgical Abstracts* are concerned, the coverage has been improved and great headway has been made in overtaking arrears. The aim of the Publication Committee has been to provide a comprehensive series of informative (and, where desirable, critical) abstracts covering the fields of knowledge of direct concern to the non-ferrous metallurgist. It has recently been decided to increase the scope of the abstracts to meet the growing needs of the metal physicist in particular, and the 1950 volume will reflect the changes that have been approved. There is general agreement throughout the world that the Institute's abstracting service is of the highest order and constitutes one of the most valuable benefits of membership.

While the size (and number of copies printed) of the Institute's publications has been growing—and growing in a marked way in recent years—the costs of production have been increasing to an extent that members may not have appreciated. The printers' rates for composing, machining, and binding had alone increased by 97 per cent. by the end of 1949 over those in force at the end of 1939, and prices have been further increased by 5 per cent. with effect from January 1950. During the same period paper and block-making costs have also been increasing.

The growing costs of the Institute's expanding services are referred to in the report of the Honorary Treasurer. The Council is considering what steps it is appropriate to take to ensure that the growth of the Institute's work shall not have to be restricted on financial grounds.

For the first time in the Institute's history, the membership at 31 December exceeded 3500. This total is capable of considerable increase, and all members are invited to take energetic steps to introduce new members from their circle of acquaintances and business and professional associates who are qualified to benefit from the Institute's work and publications.

HONORARY MEMBERS.

Professor Leslie Aitchison, D.Met., M.Sc., and Sir Clive Baillieu, K.B.E., C.M.G., M.A., have been elected Honorary Members of the Institute during the year, in recognition of their distinguished services to non-ferrous metallurgy.

FELLOWS.

Colonel Sir Paul Gueterbock, K.C.B., D.S.O., M.C., T.D., D.L., J.P., M.A., A.D.C. (Past-President), and Mr. W. H. A. Robertson (Original Member) have been elected Fellows, in recognition of their eminent services to the Institute.

MEMBERSHIP.

While the large increase in the membership for which the Council appealed has not yet taken place, the steady rate of growth of previous years has been maintained, as will be seen from the following table and the graph on p. 644 :

At 31 December	1942	1943	1944	1945	1946	1947	1948	1949
Honorary Members .	2	6	6	6	6	9	9	11
Fellows .	7	7	7	6	6	7	6	9
Ordinary Members .	1866	2018	2153	2213	2414	2491	2546	2685
Associate Members .	11	15	15	12	25	17	19	18
Student Members .	188	267	305	361	529	655	746	783
Active List .	2074	2313	2486	2598	2980	3179	3326	3506
Suspense List .	191	195	200	179	58	36	55	67
Total .	2265	2508	2686	2777	3038	3215	3381	3573

If the Institute's work is to be maintained and developed, the membership must be largely increased, and the Council therefore again appeals to members to endeavour to develop the membership among suitable persons in their own professional circles who ought to support the Institute's work and who would benefit by receiving its publications.

OBITUARY.

The Council records with regret the deaths of the following members : Dr. K. Brozyna; Miss D. P. Clapham; Dr. W. Cullen; Mr. D. H. Hopper; Mr. R. E. Horley; Mr. L. F. Keeling; Mr. G. Lenke; Mr. E. Lux; Mr. W. McGeoch; Mr. W. Paterson; Mr. W. J. Petersen; Mr. W. F. Rowden; Mr. E. A. Smith (Original Member); Mr. F. S. Tritton; and Mr. W. G. Wagner.

OFFICERS OF THE INSTITUTE.

The following members were declared elected to fill vacancies as honorary officers of the Institute with effect from the 1949 Annual General Meeting :

President :

Sir ARTHUR SMOUT, J.P.

Vice-Presidents :

Major C. J. P. BALL, D.S.O., M.C.

C. J. SMITHELLS, M.C., D.Sc.

Ordinary Members of Council :

E. A. BOLTON, M.Sc.

C. H. DAVY.

A. G. QUARRELL, Ph.D., D.Sc., A.R.C.S., D.I.C.

During the year the Council accepted, with much regret, the resignation of Professor L. Aitchison, D.Met., M.Sc., an Ordinary Member of Council, on grounds of ill-health, and, in accordance with the Articles, nominated Professor G. V. Raynor, M.A., to fill the vacancy.

HONORARY MEMBERS OF COUNCIL.

Captain (E) J. E. Cooke, R.N., has replaced Captain (E) F. A. Lister, R.N., as representative of the Lords Commissioners of the Admiralty, and Mr. L. Rotherham, M.Sc., has replaced Mr. G. L. Bailey, M.Sc., as a representative of the Institution of Metallurgists.

The Council desires to place on record its appreciation of the services of the Honorary Members of Council.

HONORARY CORRESPONDING MEMBERS TO THE COUNCIL.

The Honorary Corresponding Members to the Council who held this appointment at the beginning of the year have continued to serve, with the exception of Professor J. Neill Greenwood, D.Sc., M.Met.E. (Australia), who resigned this appointment and was succeeded by Professor H. K. Worner, D.Sc., and Dr. O. W. Ellis (Canada), who resigned and has recently been succeeded by Professor B. Chalmers, Ph.D., D.Sc., and Professor G. Letendre, Ph.D., B.A.

The Council, having reviewed the existing appointments, has elected the following additional Corresponding Members. It has been decided that these, and future, appointments shall be for a period of three years.

Belgium: H. P. A. Féron, Ing. civil Mines; *Canada*: as detailed above; *Holland*: M. Hamburger; *Italy*: L. Matteoli, Dott.chim.; *South Africa*: Professor L. Taverner, A.R.S.M., D.I.C.; *Spain*: Professor J. Orland, M.Sc., M.A., D.D.; *Sweden*: Professor A. Hultgren; *United States of America*: Professor R. F. Mehl, Ph.D., Hon.Eng.D., Hon.Sc.D., and Dr. R. A. Wilkins.

The Council desires to express its appreciation to all Corresponding Members for their help and advice during the past year, and, in particular, to Professor J. Neill Greenwood and Dr. O. W. Ellis for the services that they have rendered to the Institute as Honorary Corresponding Members to the Council since 1925 and 1924, respectively.

INSTITUTE OF METALS MEDAL.

The Institute of Metals (Platinum) Medal for 1949 was awarded to Dr. William Hume-Rothery, F.R.S., in recognition of his outstanding services to the science of non-ferrous metallurgy.

CAPPER PASS AWARD.

During the year, the first Capper Pass Award of £100 (to be made annually to the authors of papers published in the Institute's *Journal* on processes or plant used in the fabrication of non-ferrous metals) was made jointly to Messrs. C. Blazey, L. Broad, W. S. Gummer, and D. B. Thompson (Australia) for their paper on "The Flow of Metal in Tube Extrusion" (*Journal*, 1948-49, vol. 75, pp. 163-184).

PUBLICATIONS.

The number of papers published has continued to increase. During the calendar year 1949, 55 papers and addresses were printed in the *Journal*, a further 13 were published in connection with a Symposium on "Metallurgical Applications of the Electron Microscope", and one, because of its size, is included in the Monograph and Report Series (Serial No. 1206, Ruddle, "The Solidification of Castings: A Review of the Literature"), making a total of 69.

The abstracting of scientific and technical literature relating to non-ferrous metallurgy and associated subjects has been brought further up to date. The production of a decennial index to *Metallurgical Abstracts*, New Series, volumes 1-10 (1934-43) is making good progress and the index should be ready for issue at the end of 1950.

In the *Monograph and Report Series* a second printing has been made of No. 4: "An Introduction to the Electron Theory of Metals", by Dr. G. V. Raynor, and a further (seventh, revised) printing of No. 1: "The Structure of Metals and Alloys", by Dr. W. Hume-Rothery has been ordered. Other books of the series that are in the press are No. 6: "Symposium on Metallurgical Aspects of Non-Ferrous Metal Melting and Casting of Ingots for Working", and No. 7: "The Solidification of Castings: A Review of the Literature", by R. W. Ruddle. In addition, No. 8 of the series—"Symposium on Metallurgical Applications of the Electron Microscope"—should be ready for publication early in 1950.

An *Annotated Equilibrium Diagram*—No. 7 of the series—on the system beryllium-copper has been issued, and Nos. 1 to 5 (Al-Zn, Cu-Sn, Cu-Zn, Al-Cu, and Al-Mg) have again been reprinted. Others are in course of preparation by Professor G. V. Raynor and Mr. H. W. L. Phillips, respectively.

Substantial increases in the sales of publications and in the revenue from advertisements have taken place in the financial year ended 30 June 1949, the figures being (those for 1947-48 are given in parentheses): Sales of *Journal* and *Metallurgical Abstracts*, £4219 (£3791); sales of Special Publications,

£2639 (£1192); and revenue from advertisements, £4607 (£4009). Since the year 1941-42, when the figure was £761, there has been a steady annual increase in the sales of the *Journal* and *Metallurgical Abstracts*, and it is believed that the sales may still be greatly extended as the value of these publications becomes more widely known overseas and currency restrictions are relaxed.

GENERAL MEETINGS.

The Forty-First Annual General Meeting was held in London, on Wednesday, Thursday, and Friday, 30 and 31 March and 1 April 1949, one day of which was devoted to a most successful Symposium on "Metallurgical Aspects of Non-Ferrous Metal Melting and Casting of Ingots for Working". On 31 March a Dinner-Dance was held at the Savoy Hotel.

On 25 May 1948, Sir Edward Appleton, G.B.E., K.C.B., M.A., D.Sc., F.R.S., delivered the Thirty-Ninth May Lecture on "The Organization and Work of the Department of Scientific and Industrial Research".

The Forty-First Annual Autumn Meeting was held in Paris, from Monday 4 to Friday 8 October 1949, by invitation of the Société Française de Métallurgie and the French Non-Ferrous Metal Industries. The Twentieth Autumn Lecture was delivered on 3 October by Professor Georges Chaudron on "Recent French Investigations in the Field of Light Alloys". The Paris meeting was a memorable one, and was attended by about 350 members and ladies. After the meeting, parties of members visited metallurgical plants and laboratories in the areas of Issoire (Puy-de-Dôme) and Annecy and Chambéry (Haute Savoie).

STUDENTS' TOUR.

In the Easter Vacation an educational tour to metallurgical laboratories and works in the Birmingham area was organized for Student Members of the Institute. 93 Student Members took part, and 20 works and laboratories were visited. The Council records its gratitude to the Directors of the plants and laboratories visited, for their valuable co-operation in making this educational tour a success.

This tour, which was the first of its kind to be held since the war, appears to meet a real need. In view of this, further tours will be arranged for students both in Great Britain and on the Continent of Europe.

LOCAL SECTIONS.

The five Local Sections (Birmingham, London, Scottish, Sheffield, and South Wales) have been very active, and have had good programmes and, in the majority of cases, well-attended meetings. Members of the Institute continue to enjoy the privilege of free membership of the Leeds Metallurgical Society and the Manchester Metallurgical Society.

The President and Secretary have again paid visits to the Local Sections and Associated Societies and these opportunities to talk over local problems with the Committee and to meet the local members have been most valuable.

During the year two Local Section papers have been published in the *Journal*, viz., "Metals in Clock and Instrument Manufacture", by R. E. Tricker (read before the Scottish Local Section), and "Modern Billet Casting, with Special Reference to the Solidification Process", by E. Scheuer (read before the London Local Section); synopses of others have been published in the news section of the monthly issue of the *Journal*.

SPECIAL COMMITTEES.

The Metal Physics Committee has met regularly during the year and organized a very successful symposium on "Metallurgical Applications of the

Electron Microscope", which was held at the Royal Institution on 16 November 1949, in association with other societies.

A Metallurgical Engineering Committee, under the chairmanship of Mr. D. F. Campbell, M.A., A.R.S.M., has been formed to develop interest in metallurgical engineering in the non-ferrous metal industry and to promote the study of equipment and instruments used in the industrial melting, casting and working of non-ferrous materials. The Committee was instrumental in obtaining, for publication, two excellent papers on the rolling of aluminium, published in the *Journal*, 1949, vol. 75, pp. 899-948.

STAFF.

The increased activities of the Institute and the enlarged publication programme during the year under review have again made heavy demands on the staff, and the Council desires to place on record its high appreciation of all the good work accomplished.

During the year the Council appointed Mr. N. B. Vaughan, M.Sc., F.I.M., as Editor of Publications, to succeed Major W. G. Askew, M.C., A.I.M., who resigned. Members will recall that Mr. Vaughan served on the staff (1938-46) as Assistant Editor, and his present appointment as Editor is intended to free the Secretary from editorial work, as set out in the Council's Report of 1947.

JOINT ACTIVITIES.

JOINT LIBRARY AND INFORMATION DEPARTMENT.

The sphere of usefulness of the Joint Library continues to extend and members are availing themselves more and more of the organization. Increasing use has also been made of the Library by Government Departments, Research Associations, Universities, and other teaching establishments. During the past year 10,523 publications were borrowed, as compared with 10,041 in 1948. The number of textbooks added was 350, many of these by presentation, and the Council thanks those who have presented volumes to the Library.

Members are reminded that the use of the Lending Library is a valuable privilege of membership. Books and periodicals are sent post free to members resident in Great Britain. In addition to the books filed in the Joint Library, members may borrow through the Librarian, Mr. R. Elsdon, publications from the Science Library at South Kensington. Assistance is also given to all members, in Great Britain and overseas, to obtain photostat copies of articles which can be supplied under certain conditions. 89 photostat copies and 38 microfilms were supplied to members during the past year.

The work of the Information Department is an important part of the service. The Department is prepared to answer scientific and technical enquiries from members, but it is not its function to give the type of advice which comes within the field of the metallurgical consultant.

JOINT COMMITTEE ON METALLURGICAL EDUCATION.

Mr. E. G. Lawford agreed to become Chairman of the Joint Committee on Metallurgical Education on the retirement, owing to ill-health, of Professor Leslie Aitchison.

During the year two Sub-Committees were formed to investigate metallurgical education at Universities and Technical Colleges.

Categories of employment have been divided into (1) managerial; (2) research; (3) technical; and (4) operatives. In considering the appropriate metallurgical training for these categories, it was decided that consideration should first be given to existing provisions in metallurgical education to see how far these were appropriate to the standard and requirements of each category.

It was decided to proceed first with the investigation into University courses and, as a first step, enquiries were directed to the teachers of metallurgy at Universities and to a widely representative selection of employers in the metallurgical industries. Long and carefully considered replies have been received from all the Universities consulted and from over 90 individuals in industry, and these replies in many cases embody the views of several individuals and groups. They are being studied by a working party with a view to the preparation of a considered statement of the position by the Subcommittee and Committee.

JOINT COMMITTEE FOR NATIONAL CERTIFICATES IN METALLURGY.

The Joint Committee for National Certificates in Metallurgy, in which the Institute shares responsibility with the Ministry of Education and The Iron and Steel Institute, Institution of Mining and Metallurgy, and The Institution of Metallurgists, reports that satisfactory progress has been made during the year 1948-49.

Approved schemes for senior courses leading to an Ordinary National Certificate in Metallurgy were in operation at 22 technical colleges (compared with 18 during the previous year) and schemes for advanced courses leading to a Higher National Certificate at 11 colleges (compared with 9 during the previous year).

Final examinations for the Ordinary National Certificate were held during 1949 at 21 technical colleges and for the Higher National Certificate at 10 technical colleges (compared with 15 and 8, respectively, during 1948). The number of candidates for the Ordinary National Certificate increased from 123 in 1948 to 221 in 1949 and for the Higher National Certificate from 38 in 1948 to 75 in 1949. There has also been a substantial increase in the number of students entering the first and second years of the courses.

Applications for approval of schemes have been received from a number of colleges and, if approved by the Joint Committee, this will result in courses being available to students in other districts.

MOND NICKEL FELLOWSHIPS COMMITTEE.

Mond Nickel Fellowships were awarded to the following in 1949 :

Mr. J. Monaghan (Stewarts and Lloyds, Ltd.) to study the method of control and administration of basic open-hearth operation and practice in the steel industry in U.S.A.

Mr. R. Stewartson (United Steel Companies, Ltd.) to study the design and operation of modern hot-rolling mill plant in U.S.A.

Mr. E. Brunskill (Mufulira Copper Mines, Ltd.) to study the metallurgical practice in the mining, smelting, and refining of non-ferrous metals in Africa, with special reference to copper and related metals.

APPENDIX.

COMMITTEES.

The main Committees of the Institute which have served during the year were constituted as follows on 31 December 1949 :

Finance and General Purposes Committee.

Major C. J. P. Ball (*Chairman*).
Mr. D. F. Campbell.
Lieut.-Colonel Sir John Greenly.
Sir William Griffiths.
Colonel Sir Paul Gueterbock.
Mr. H. W. G. Hignett.
Dr. J. W. Jenkin.

Professor A. J. Murphy.
Mr. D. P. C. Neave.
Mr. H. S. Tasker.

Ex-officio :

Sir Arthur Smout (*President*).
Mr. W. A. C. Newman (*Honorary Treasurer*).
Professor H. O'Neill (*Chairman, Publication Committee*).

Local Sections Committee.

Mr. H. W. G. Hignett (*Chairman*).
 Dr. W. O. Alexander.
 Mr. L. E. Benson.
 Dr. J. C. Chaston.
 Mr. W. J. G. Cosgrave.
 Dr. J. E. Garside.
 Professor A. Preece.

Representatives of Local Sections :

Mr. R. Chadwick (*Birmingham, Chairman*).
 Mr. E. H. Bucknall (*Birmingham, Hon. Secretary*).
 Mr. W. F. Randall (*London, Chairman*).
 Dr. E. C. Rhodes (*London, Hon. Secretary*).
 Mr. A. Craig Macdonald (*Scottish, Chairman*).
 Mr. M. Hay (*Scottish, Hon. Secretary*).
 Mr. H. G. Dale (*Sheffield, Chairman*).
 Dr. W. R. Maddocks (*Sheffield, Joint Hon. Secretary*).
 Mr. D. W. Hopkins (*South Wales, Chairman*).
 Mr. K. M. Spring (*South Wales, Hon. Secretary*).

Ex-officio :

Sir Arthur Smout (*President*).
 Mr. W. A. C. Newman (*Honorary Treasurer*).

Medal Committee.

Sir Arthur Smout (*President*) (*Chairman*).

Ex-officio :

President-Elect.

Ordinary Members :

Not more than four medallists who are, or have been, Members of Council, to be selected by the President.

Metallurgical Engineering Committee.

Mr. D. F. Campbell (*Chairman*).
 Major C. J. P. Ball.
 Mr. D. P. C. Neave.
 Mr. W. J. Thomas.

Ex-officio :

Sir Arthur Smout (*President*).
 Professor H. O'Neill (*Chairman, Publication Committee*).

Metal Physics Committee.

Dr. N. P. Allen (*Chairman*).
 Dr. Maurice Cook.
 Dr. R. F. Hanstock.
 Mr. H. W. G. Hignett.
 Dr. W. Hume-Rothery.
 Mr. R. King.
 Mr. F. R. N. Nabarro.
 Mr. D. A. Oliver (*representing the Iron and Steel Institute and the British Iron and Steel Research Association*).
 Dr. E. Orowan.
 Dr. A. G. Quarrell.
 Professor G. V. Raynor.
 Dr. T. Ll. Richards.
 Mr. L. Rotherham.
 Dr. C. J. Smithells.

Ex-officio :

Sir Arthur Smout (*President*).
 Professor H. O'Neill (*Chairman, Publication Committee*).

Nominations Committee.

Sir Arthur Smout (*President*) (*Chairman*).
 Sir William Griffiths.
 Colonel Sir Paul Gueterbock.

Publication Committee.

Professor H. O'Neill (*Chairman*).
 Mr. G. L. Bailey.
 Dr. Maurice Cook.
 Mr. C. H. Davy.
 Dr. F. A. Fox.
 Mr. T. M. Herbert.
 Mr. F. Hudson.
 Mr. J. F. B. Jackson.
 Dr. Ivor Jenkins.
 Mr. E. A. G. Liddiard.
 Mr. A. Glynne Lobley.
 Mr. H. W. L. Phillips.
 Professor G. V. Raynor.
 Mr. Christopher Smith.
 Professor F. C. Thompson.
 Dr. L. R. Underwood.

Ex-officio :

Sir Arthur Smout (*President*).
 Major C. J. P. Ball (*Chairman, Finance and General Purposes Committee*).
 Mr. W. A. C. Newman (*Honorary Treasurer*).
 Mr. D. F. Campbell (*Chairman, Metallurgical Engineering Committee*).
 Dr. N. P. Allen (*Chairman, Metal Physics Committee*).

REPORT OF THE HONORARY TREASURER

for the Financial Year Ended 30 June 1949.

The accounts of the Institute for the financial year 1948-49 reflect, in general, its increased activities, especially in publication. The excess of income over expenditure last year (£883)—attributable then mostly to enhanced sales of publications—has not been maintained, with the result that this year the Institute is £864 overspent, an outcome which was not unforeseen. This sum is made up of £557, the actual difference on the year's working, and £307, a net sum written off following a recent adjustment of the membership list by the Council and the elimination of all doubtful cases in order to make it real. The subscriptions now outstanding, amounting to £489, are considered to be reasonably good debts and hence the reserve against possible defaults this year has been reduced from £150 to £50.

A change over of £1440 (i.e. £864 + £557) may be considered not excessive in view of the Institute's expansion, the avowed decision of the Council to maintain the publication of all papers sanctioned by the Publication Committee, and the vigour with which the Institute is pursuing its policy of being of the utmost service to its members. The deficiency of £864 will be met by a transfer from the War-Time Emergency Fund, which thereafter will stand at £4519. Of this sum, however, roughly one third is currently employed in financing publications in advance. The fund amounted to a maximum of £7767 in 1946, so that in three years it has been reduced by £3248, or 42%.

The net increase in income amounts to £2664 and the net increase in expenditure to £4411. The net decrease in surplus since 1947-48 is therefore £1747, £598 occurring in the general and £1149 in the publication account.

The increase in income is due mainly to (a) the net increase in membership during the year; (b) the greatly expanded sales of publications; and (c) greater revenue from advertisements. The monetary value of the increase in membership is £380 (3.4%), a very low proportion, and of sales of publications and revenue from advertisements £2473 (27.5%).

The biggest increases in expenditure are due partly to rises in salaries and wages and increases in staff, but most of all, to the increased cost of the Institute's expanded publications. Forseeable additions to expenditure during the next few years make it imperative that (a) income is considerably augmented and/or (b) some effort is made to review critically the whole field of expense.

The excess of expenditure over income in the case of the *Journal* is £1386, as compared with an excess of income last year of £352. For Special Publications last year's excess of income, £324, has mounted this year to £914. In total, therefore, a balance of income of £678 has given place to a deficiency of £472, a change over of £1150.

Following is an analysis of the financial side of the Institute's publications, showing the relative actual and percentage increases in income and expenditure. It should be borne in mind, however, that transactions in regard to Special Publications are necessarily subject to great fluctuations, and are governed by the timing and conditions of issue of comparatively few volumes.

INCOME.

Monthly Journal and Metallurgical Abstracts :

Increase in sales	£428	(13%)
„ „ advertisement revenue	£598	(15%)
„ overall	£1026	(13%)

Special Publications :

Increase in sales	£1447	(121%)
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EXPENDITURE.

Monthly Journal and Metallurgical Abstracts :

Increase in composition, paper, and printing.	£2069	(37%)
„ „ blocks and drawings	£125	(45%)
„ „ postage, packing, &c.	£279	(37%)
„ „ abstractors' and reviewers' fees	£166	(45%)
„ overall	£2764	(37%)

Special Publications (the biggest item was Monograph and Report Series No. 5—Symposium on Internal Stresses in Metals and Alloys) :

Increase overall	£859	(99%)
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The number of papers published has been much larger than usual, some being of more than average length and others profuse with diagrams and illustrations. While a peak of publication was expected after the lean war years, it appears now that the steady level will probably be higher than in the years prior to 1939, owing principally to a greater number of people being engaged in research in a larger number of laboratories, and to expansion of the Non-Ferrous Metals Industry. In these circumstances it may be expected that, while costs of publication may ultimately recede, they will never again be comparable with those of pre-war days.

It may be remarked, in passing, that this year the sales of publications and of advertisement space account for 47% of the total income, and that, of this percentage, sales of Special Publications alone amount to 10·8%. These proportions are less stable than that of members' subscriptions, and may vary widely. The maintenance of the Institute's activities would be enhanced considerably and given a much firmer basis by an increase in membership. The increases in membership attained recently have not provided the constantly increasing revenue required to meet the expansion in the Institute's services.

The Balance Sheet indicates a net decrease in assets of £661. The reserves are maintained at approximately the same figure as last year.

There has been no change during the year in either the nature or the amount of the securities held. A decrease in market value is apparent and that loss may increase, but it is hoped that variations in the day-to-day prices of the various stocks will be comparatively slight. The bulk of the stock was purchased with that end in view.

Reference must be made to the fact that £477 in the General Fund Account and £3150 in the Mond Nickel Fellowships Account, representing in each case returned income tax which has hitherto been received regularly, have been included, although these sums are not yet in the Institute's possession. Their payment depends on the Commissioners' interpretation of the rulings given in two recent Court decisions and its bearings in relation to the Institute's constitution.

In common with all societies whose membership is of moderate dimensions but whose aspirations to help as far as possible in the development of industry and research are high, the Institute is passing through times that might prove difficult unless carefully watched. It is possessed of great vitality, however, and its prestige must grow. The solution of ancillary problems will follow.

THE INSTITUTE
BALANCE SHEET AS

30.6.48.	£	£		£	s.	d.	£	s.	d.
			RESERVES.						
	21,294		<i>Endowment Fund</i>	21,294	9	10			
	10,000		<i>General Reserve</i>	10,000	0	0			
	4,367		<i>Entrance Fees</i>	4,472	18	5			
35,661							35,767	8	
			CURRENT SURPLUSES.						
			<i>Accumulated Fund:</i>						
	7,393		Balance as at 30 June 1948	3,026	11	7			
			Amount transferable from War-time Emergency						
			Fund	864	0	7			
				3,890	12	2			
				£	s.	d.			
			<i>Less Excess of Expenditure over</i>						
			Income for the year	864	0	7			
883			<i>Excess Income</i>	—					
	5,000		<i>Transfer to Reserve</i>	—					
	8,276								
		250	<i>Transfer to Investment Redemption</i>						
			Reserve	250	0	0			
5,250				1,114	0	7			
	3,026			£	s.	d.			
	5,287		<i>War-Time Emergency Fund</i>	5,383	6	11			
			<i>Less amount transferable to General</i>						
			<i>Funds.</i>	864	0	7			
				4,519	6	4			
750			<i>Special Publication Reserve</i>	750	0	0			
250			<i>Investment Redemption Reserve</i>	500	0	0			
9,313				8,545	17	11			
44,974							44,313	6	
			CURRENT LIABILITIES.						
	1,552		<i>Sundry Creditors</i>	3,498	17	8			
	398		<i>Lloyds Bank</i>	—					
	487		<i>Subscriptions in Advance</i>	410	16	5			
2,437				3,909	14				
			SPECIAL FUNDS.						
	13,859		<i>Mond Nickel Fellowship Fund</i>	16,846	0	0			
	200		<i>Copper Pass Fund</i>	257	17	6			
14,059				17,103	17				

NOTE.—The Settlement of claims for refund of Income Tax amounting to £177 7s. 3d. for the Institute's General Funds and £3,150 for the Mond Nickel Fellowships Fund included in the Accounts, has been postponed by the Inland Revenue pending their decision on the effect of two High Court cases.

REPORT TO THE MEMBERS OF THE INSTITUTE OF METALS.

We have audited the above Balance Sheet dated 30 June 1949, and the annexed Income and Expenditure Account for the year ended 30 June 1949, and report that we have obtained all the information and explanations which to the best of our knowledge and belief were necessary for the purposes of our audit.

In our opinion, proper books of account have been kept by the Institute, so far as appears from our examination of those books.

The above-mentioned Balance Sheet and annexed Income and Expenditure Account are in agreement with the books of Account. In our opinion, and to the best of our information, and according to the explanations given us, the said Accounts give the information required by the Companies Act 1948, in the manner so required, and give a true and fair view, in the case of the Balance Sheet, of the state of the Institute's affairs as at 30 June 1949, and in the case of the Income and Expenditure Account of the excess of expenditure over income for the year ended 30 June 1949.

POPPLETON & APPELEY,
CHARTERED ACCOUNTANTS,
BIRMINGHAM AND LONDON.

26 September 1949.

Approved on behalf of the Council:

ARTHUR SMOUT, *President.*
W. A. C. NEWMAN, *Honorary Treasurer.*
O. J. P. BALL, *Chairman, Finance and General Purposes Committee.*
S. C. GUILLAN, *Secretary.*

£61,470

£65,326 17 9

OF METALS.

AT 30 JUNE 1949.

10.6.48.

£	£	£	£	s.	d.	£	s.	d.
			FIXED ASSETS.					
			<i>Office Furniture and Equipment:</i>					
	1		Nominal value as at 30 June 1947			1	0	0
	326		Additions since, at cost			401	5	6
		327				402	5	6
		21				93	5	9
306			Less Depreciation to date					
								308 19 9
			<i>Library Books, &c.:</i>					
	1		Nominal value as at 30 June 1947			1	0	0
307								309 19 9
			INVESTMENTS AND FUNDS.					
			<i>General Fund:</i>					
	16,301		Securities at cost, per schedule	16,301	7 11			
			(Market value £15,829 10s. 11d.)					
	32		Lloyds Bank, Ltd., Deposit Account	66	15 9			
	5		Post Office Savings Bank					
16,338						16,368	3 8	
			<i>Endowment Fund:</i>					
	21,292		Securities at cost, per schedule	21,292	7 4			
			(Market value £20,688 14s. 6d.)					
	2		Lloyds Bank, Ltd., Deposit Account	2	2 6			
21,294						21,294	9 10	
			<i>War-Time Emergency Fund:</i>					
	2,855		Securities at cost, per schedule	2,855	0 0			
			(Market value £2,811 10s. 8d.)					
	962		Lloyds Bank, Ltd., Deposit Account	25	5 2			
	7		Post Office Savings Bank	476	1 2			
	569		Lloyds Bank, Ltd., Current Account	533	19 4			
	—		London Trustee Savings Bank	504	3 4			
	887		Payments in advance for publications	954	4 1			
	7		Sundry debtors	34	13 10			
	5,287					5,383	6 11	
42,919								43,046 0 5
			CURRENT ASSETS.					
	1		<i>Publications, &c., at nominal value</i>			1	0	0
	961		Debtors: Subscriptions	488	19 5			
	68		„ Entrance Fees					
	1,029							
	151		Less Provision for doubtful subscrip- tions	50	0 0			
	878					438	19 5	
	3,306		Sundry debtors and payments in ad- vance	2,652	5 10			
	4,184					3,091	5 3	
4,185								
	—		Cash at Lloyds Bank, Ltd.	1,762	12 4			
	—		Cash in hand	12	2 6			
						1,774	14 10	
								4,867 0 1
			INVESTMENT OF SPECIAL FUNDS.					
			<i>Mond Nickel Fellowships Fund:</i>					
	5,000		Abbey National Building Society	5,000	0 0			
	1,250		Halifax Building Society	1,250	0 0			
	1,250		Co-operative Permanent Building Society	1,250	0 0			
	500		Post Office Savings Bank	1,008	6 8			
	500		London Trustee Savings Bank	1,007	5 10			
	2,209		Lloyds Bank, Ltd., Deposit Account	4,087	9 10			
	—		„ „ Current Account	23	14 6			
	3,150		Income Tax Recoverable	3,150	0 0			
	—		Sundry Debtors	69	3 2			
	13,859					16,846	0 0	
			<i>Copper Pass Fund:</i>					
	200		Post Office Savings Bank	255	0 0			
	—		Sundry Debtors	2	17 6			
	14,059					257	17 6	
								17,103 17 6

THE INSTITUTE OF METALS. INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 30 JUNE 1949.

EXPENDITURE.		INCOME.	
£	s. d.	£	s. d.
30,643.		30,648.	
ESTABLISHMENT EXPENSES:		SUBSCRIPTIONS AND DONATIONS	
878	870 18 6	11,253	11,653 3 6
150	135 14 0	INTEREST ON INVESTMENTS	
171	70 4 5	<i>(Gross):</i>	
1,199	1,076 16 11	General Fund (including Tax £140 7s. 7d.)	
ADMINISTRATION EXPENSES:		Endowment Fund (including Tax £392 13s. 6d.)	
6,111	6,944 16 0	RESERVE FROM PREVIOUS YEAR	
610	748 8 7	<i>NOT REQUIRED</i>	
516	516 0 0	Profit Sale of Investments	
639	582 11 8	1,265 6 10	
681	718 6 7		
109	109 0 8		
49	29 7 5		
37	52 10 0		
143	162 4 6		
280	316 10 3		
143	96 19 11		
9,323	10,276 15 7		
JOURNAL AND METALLURGICAL ABSTRACTS:		JOURNAL AND METALLURGICAL ABSTRACTS:	
7,617	10,300 19 0	3,791	4,218 19 11
SPECIAL PUBLICATIONS:		4,009	4,607 3 6
866	1,725 3 5	7,800	8,826 3 5
MEETINGS, GRANTS, JOINT ACTIVITIES, &c.:		1,192	2,639 5 5
92	111 7 10	8,992	11,465 8 10
361	394 1 11		
500	500 0 0		
169	231 7 0		
250	125 0 0		
50	50 0 0		
25	25 0 0		
81	24 3 0		
1,548	1,460 19 9		
BAD AND DOUBTFUL SUBSCRIPTIONS:			
—	50 0 0		
—	307 0 10		
—	357 0 10		
—	46 17 2		
—	71 17 1		
330	—		
21	—		
883	—		
£21,787	£21,787		

* No establishment or administrative expenses are included in these costs.

EXCESS OF EXPENDITURE OVER INCOME FOR THE YEAR.

THE INSTITUTE OF METALS.
FUNDS ACCOUNTS FOR THE YEAR ENDED 30 JUNE 1949.

ENDOWMENT FUND.

EXPENDITURE.		INCOME.	
£	s. d.	£	s. d.
30,648.			
To Transfer to General Funds: Investment Interest	768 14 7	By Balance at 30 June 1948	21,294 9 10
638		" Interest on Investments and Bank Interest (including	768 14 7
21,294		" Tax £322 13s. 6d.)	---
		" Profit on Sale of Investments	---
			£22,063 4 5
£21,932			

WAR-TIME EMERGENCY FUND.

£	s. d.	£	s. d.
11		5,144	
To Bank Charges		By Balance at 30 June 1948	5,286 16 11
" Amount transferable to General Funds	864 0 7	" Interest on Investments and Bank Interest (including	96 11 4
5,287		" Tax £14 6s. 2d.)	---
			£5,383 8 3
£5,298			

MOND NICKEL FELLOWSHIPS FUND.

£	s. d.	£	s. d.
61		7,000	
To Grants	4,007 17 8	By Balance at 30 June 1948	13,858 11 8
" Professional Charges re Deed of Covenant, &c.	134 12 6	" Donation Received (including Tax £3,150)	7,000 0 0
Stamp Duty	---	" Interest	172 9 5
Applicants' Travelling Expenses	25 12 8		---
Sundry Expenses	9 16 0		---
Bank Charges	7 2 3		---
" Balance at 30 June 1949	16,846 0 0		---
13,859			£21,031 1 1
£14,028			

CAPPER PASS FUND.

£	s. d.	£	s. d.
200		200	
To Grants	150 0 0	By Balance at 30 June 1948	200 0 0
" Balance at 30 June 1949	257 17 6	" Donation Received	200 0 0
		" Bank Interest	7 17 6
			£407 17 6
£200			

W. H. A. ROBERTSON FUND.

£	s. d.	£	s. d.
---		---	
To Design of Medal	100 0 0	By Donation Received	100 0 0
			£100 0 0

THE INSTITUTE OF METALS.

SCHEDULE OF SECURITIES, 30 JUNE 1949.

£	£		£	s.	d.	£	s.	d.
30,648.		<i>General Fund:</i>						
	5,500	£5,500 3% Savings Bonds, at cost	5,500	0	0			
	1,010	£1,010 2½% Treasury Stock, at cost	1,010	0	0			
	4,734	£4,359 4% Consolidated Stock, at cost	4,734	6	11			
	5,057	£5,000 2½% National War Bonds, at cost	5,057	1	0			
16,301						16,301	7	11
		<i>Endowment Fund:</i>						
	525	£525 2½% Defence Bonds, at cost	525	0	0			
	1,285	£1,285 3% Savings Bonds, at cost	1,285	0	0			
	19,482	£17,926 4% Consolidated Stock, at cost	19,482	7	4			
21,292						21,292	7	4
		<i>War-Time Emergency Fund:</i>						
	500	£500 2½% Defence Bonds, at cost	500	0	0			
	375	500 15s. War Savings Certificates, at cost	375	0	0			
	150	150 £1 War Savings Certificates, at cost	150	0	0			
	950	£950 2½% National War Bonds, at cost	950	0	0			
	880	£795 4% Consolidated Stock, at cost	880	0	0			
2,855						2,855	0	0
<u>£40,448</u>						<u>£40,448</u>	<u>15</u>	<u>3</u>

DISCUSSION ON THE PAPER BY MR. H. J. V. TYRRELL: "SOME ASPECTS OF THE PRODUCTION AND HEAT-TREATMENT OF ELECTROLYTIC COPPER POWDER."

(*J. Inst. Metals*, this vol., p. 17.)

DR. G. E. GARDAM,* B.Sc., A.R.C.S., F.I.M. (Member): It was shown in a paper by Hothersall and myself † that copper powder could be produced by electrolysis of a strongly acid copper sulphate solution at a high current density, but that the powder, if simply washed and dried, quickly darkened. If, however, the powder, after water washing, was further washed with an alkaline solution, such as dilute sodium carbonate, and then with water, it was quite stable after filtering and vacuum drying, and had a much smaller oxide content. No experiments on annealing the product were carried out, and indeed the powder seemed quite satisfactory as prepared. A complete scheme for a pilot-plant size unit was worked out in this paper.

The AUTHOR (*in reply*): I had the privilege of reading Dr. Gardam's report during the course of the work described in my paper, though I was not aware of its subsequent publication. The method of washing suggested was tried on the pilot plant, and was said to make no difference to the stability of the vacuum-dried product. The latter, as stated in my paper, contained some oxide but did not, in general, oxidize further on storage. It was not suitable for use in powder metallurgy, and the annealing process was introduced in an attempt to improve its metallurgical properties. The unstable powders referred to in my paper were, without exception, annealed powders.

To sum up, I would agree with Dr. Gardam about the stability of adequately washed, vacuum-dried powders; dispute his claims concerning the necessity of an alkaline wash and the satisfactory properties of unannealed powders; and suggest that, in my experience, the design of an economic plant for the production of metal powders is more difficult than would appear from Dr. Gardam's paper.

* Director, Design and Research Centre for the Gold, Silver, and Jewellery Industries, London.

† *J. Electrodepositors' Tech. Soc.*, 1945, 20, 61.

DISCUSSION ON THE PAPER BY MR. L. E. SAMUELS: "THE METALLOGRAPHY OF COPPER CONTAINING SMALL AMOUNTS OF BISMUTH."

(*J. Inst. Metals*, this vol., p. 91.)

MR. D. WHITWHAM,* M.A. (Junior Member): Apart from their special contribution to the understanding of copper embrittlement, Mr. Samuels's experiments direct attention to the more general difficulty of distinguishing a boundary channel from a boundary precipitate and, by implication, a small pit from a minute particle. The extension of conventional surface examination to an examination of the etched section will therefore be much appreciated by metallographers. In resolving this difficulty, the work also lays bare another problem, which for the microscope appears insoluble, namely that of deciding "what was in the hole, from what is not there any more".

In the course of researches on aluminium-4% copper alloy,† both grain-boundary embrittlement and a susceptibility to intercrystalline corrosion in sodium chloride solution were found to occur at a stage of ageing at which no particles could be resolved. In this case also, there is the possibility of differences of composition in the solid solution of the type favoured by the author, but a second explanation is possible and appears better in some respects.

Briefly, crystal dissolution may be regarded as a process of "negative crystallization" which, in certain circumstances, may begin only at certain points and extend from these points—the formation of etch-figures is such a case. In the case of boundary attack, it is necessary to assume that there is some special reason for attack to start, e.g. a monatomic layer of impurity atoms, a concentration of lattice defects, or an "atmosphere" of impurity atoms associated with such defects. Extension of attack would then appear to be governed by crystallographic factors; by the relative ease with which atoms may be removed from the exposed edges (or faces) of the two adjacent crystals. Such a chemical anisotropy would account for the geometrical shape of the boundary channel, whilst the concept of a gradation of attack controlled by the concentration gradient of impurity atoms would presumably result in a smooth, curved contour.

Increasing use of radioactive tracer and microradiographic techniques may provide confirmatory evidence of one idea or the other in the near future, but the microscope is clearly unsuitable for the detection of monatomic layers, and probably also of minor differences of composition within a solid solution.

The AUTHOR (*in reply*): I agree with Mr. Whitwham that the present investigation has emphasized the difficulty in positively identifying a boundary precipitate by microscopic inspection of the surface. One cannot help wondering whether other instances have occurred where features reported as

* Laboratoire du Centre National de la Recherche Scientifique, Vitry-sur-Seine, France.

† Research carried out in the Corrosion Laboratory, Cambridge University.

fine precipitates may not, in fact, have been etched channels or pits. It is of interest here to note that, of the four means of investigation previously applied to this particular type of problem (normal optical microscope, phase-contrast microscope, interference optical microscope, and electron microscope), the interference optical microscope appears to have given the most definite and unambiguous interpretation of the nature of the "dark lines".

Mr. Whitwham's alternative explanation of the mechanism of etching of the boundary channel is of great interest. It should be noted, however, that in this particular instance there appears to be a correlation between the etching of a boundary channel and the presence of a concentration gradient, irrespective of the actual mechanism of etching. The grain boundaries vary markedly with respect to etching behaviour but very little with respect to brittleness; etching presumably occurs only at those grain boundaries where the bismuth concentration is relatively high and where a concentration gradient would be present.

DISCUSSION ON THE PAPER BY DR. E. SCHEUER: "MODERN BILLET CASTING, WITH SPECIAL REFERENCE TO THE SOLIDIFICATION PROCESS."

(*J. Inst. Metals*, this vol., p. 103.)

The AUTHOR: Since the paper appeared, two communications have been received from abroad which supplement and correct statements contained in it. Mr. Irving Rossi, of the Rossi Continuous Casting Co., Inc., New York, considers that somewhat too great caution has been shown in the remarks regarding the application of the continuous-casting process to high-melting-point alloys. Mr. Rossi states that his firm have built a number of continuous-casting machines which have been successfully used for casting aluminium, brass, copper, and steel.

Dr. Francis C. Frary, Director of Research of the Aluminum Company of America, states that since several years before the war billets of high-strength aluminium alloys have been produced in the Company's works exclusively by the continuous-casting process. This would seem to represent the first case of industrial development and large-scale application of the process. He regards the statement in the paper regarding the Hazelett roller-casting machine as too favourable. Large-scale tests with this machine have, in his experience, proved disappointing.

MR. W. A. BAKER,* B.Sc., F.I.M. (Member): Dr. Scheuer has given us an excellent account of the general principles involved in modern billet casting. I would like to ask him for a little further information on two points involved in semi-continuous casting processes.

The most striking feature of the popular short-sleeve-mould method is its apparent simplicity, although, as is clear from Dr. Scheuer's paper, many points of detail must be closely controlled to get successful results. The process has not yet been applied to copper-base alloys to the same extent as to light alloys, and I would welcome Dr. Scheuer's view on how far this is due to technical difficulties. Most of the copper-base alloys are very ductile in comparison with high-strength light alloys, and one would not expect to encounter serious difficulties with internal stress in the semi-continuously-cast products. On the other hand, the majority of the alloys do not form refractory and tenacious oxide films like that formed on light alloys, and I wonder if for this reason they give more trouble with mould friction than the light metals do. Dr. Scheuer makes no reference to this factor in his brief account of the semi-continuous casting of light alloys. I should be interested to know whether he thinks that the oxide film has a useful effect in reducing direct contact between the molten metal and the mould, thereby minimizing friction.

One of the major problems referred to by Dr. Scheuer is that of high internal stress in semi-continuously-cast, high-strength light alloys. On the face of it these stresses might be minimized in two diametrically opposed ways. The ideal way is to extract most of the heat from the solidifying metal in a

* Senior Metallurgist, British Non-Ferrous Metals Research Association, London.

direction parallel with the axis of the billet, thereby reducing thermal stress to a minimum in all parts of the casting. The difficulty here is that the thermal conductivity of the metal is not high enough to make this possible in large-scale practice. The alternative possible method is to cool drastically the mould and the adjacent parts of the emerging ingot, but to refrain from further cooling of the lower part of the ingot so that in the latter region there is an opportunity for temperature gradients to be minimized by transverse conduction before the metal reaches such low temperatures that the thermal stresses are not relieved by relaxation. The disadvantage of this method is that less heat is extracted from the solidifying mould in the direction of the axis of the billet, with the result that the isotherms in the solidifying mass, and in the adjacent solid metal, are even more likely to produce internal stresses. However, the temperature measurements published by Doyle * in 1945 suggest that something might be done to lessen internal stresses in this way. His measurements showed that the greater part (70%) of the heat content of the metal was extracted by the cooling water applied to the sleeve mould and to the first foot or so of the emerging billet. The axial temperature gradients in the lower part of the ingot were relatively flat, showing that conduction of heat in this direction through the lower part of the ingot made a relatively small contribution to the total heat extraction. It is possible, therefore, that if the cooling water was deflected from the ingot surface at a level a foot or so below the mould, the internal stresses in the casting might be considerably lowered by transverse conduction below this level, and I would like to have Dr. Scheuer's views on the prospect of minimizing the difficulty in this way.

DR.-ING. P. BRENNER † (Member): Dr. Scheuer points out that the microstructure of continuously-cast billets shows a fine distribution of constituents, while billets cast in an upright mould exhibit microporosity and a relatively coarse distribution of micro-constituents. Dr. Kostron and I have recently investigated, ‡ by microhardness tests, macro- and micro-segregation in continuously-cast and chill-cast ingots of two aluminium alloys. We found the amount of macro-segregation to be much lower in the continuously-cast ingots; whereas the differences in concentration within the grains were almost the same in the continuously-cast and chill-cast ingots in the as-cast condition. If, however, the ingots were soaked at the homogenizing temperature, micro-segregation was removed much more rapidly from the continuously-cast ingots as a consequence of the smaller grain-size and the finer distribution of eutectic in the interdendritic network. This is of considerable practical importance, as the continuously-cast ingots can be given a much shorter homogenization treatment than the chill-cast ingots (the ratio is about 1 : 20).

Mention may be made of a process which combines continuous casting and continuous rolling (see Fig. A, Plate CII), developed by the Junghans Company during the past few years. When the solidified billet leaves the mould it is not allowed to cool to room temperature but is immediately hot rolled and then cold rolled. In the Junghans plant a hot-rolling mill is placed directly below the water-cooled mould and reduces the 4-in.-dia. billet to strip $\frac{3}{8}$ in. thick (see Fig. B, Plate CIII). A photomacrograph of a longitudinal section of the strip taken at this point appears in Fig. C (Plate CIII). The hot rolling is followed by cold rolling which reduces the thickness of the strip to $\frac{1}{8}$ in.

Pure aluminium (99.5%) strip produced in this plant had good mechanical properties, but the surface was comparatively rough as a result of insufficient

* W. M. Doyle, *Metal Ind.*, 1945, **66**, 370, 390.

† Vereinigte Leichtmetallwerke G.m.b.H., Hannover-Bonn, Germany.

‡ *Metallurgia*, 1950, **41**, (244), 209.

cooling of the rolls. Apart from this problem, which has still to be solved, the plant is very expensive and the process would therefore probably only be practicable for the production of large quantities of strip of the same size.

As Dr. Scheuer states, the continuous-casting process to-day is not confined to aluminium and magnesium alloys and in Germany it is regularly being used for copper, brass, and zinc ingots. For copper and copper alloys, the fully-continuous-casting process with direct cooling (short-mould method) is also used.

In the continuous casting of steel good progress has been made during the past few years. In a pilot plant in Germany nearly 700 tons of low-carbon steel were continuously cast last year. Billets up to 10 in. in dia. showed a fine, dense structure and extremely small segregation of carbon, phosphorus, and sulphur. The rolling qualities were very satisfactory and the mechanical properties well above those specified for steel produced in the ordinary way. On the strength of these results, the Mannesmannröhren-Werke, Düsseldorf, the Hüttenwerke Hückingen A.G., and the Westdeutsche Mannesmannröhren A.G. have decided to adopt the continuous-casting process for the production of seamless steel tubes. The new plant will be completed shortly.

DR. W. M. DOYLE,* M. Eng., F.I.M. (Member): In the early days of continuous casting, now the generally accepted practice as far as light alloys are concerned, progress proceeded by a system of trial and error, lacking the benefit of the mathematical analyses published by Péloutier † and Bingel ‡ during the last few years. Most of the early problems were engineering ones due to the lack of positive and reliable speed-control mechanisms and instruments reading to within 0.1 in./min. at speeds in no case greater than about 9 in./min. Notwithstanding a certain earlier enthusiasm for casting at too high a speed, it is remarkable how good is the agreement between the speeds and cooling-water conditions developed on an *ad hoc* basis, and those now calculated for casting billets of various dimensions in the different aluminium alloys.†

Although Dr. Scheuer's excellent review is general in character, the major development has taken place in the casting of aluminium alloys and, in this connection, it would have been very interesting if he had included a résumé of his own experiences. For instance, he could have enlarged upon the limitations of the continuous-casting process to which he refers on p. 119 of the paper. It must be admitted that certain compositions for the very high-strength alloys conforming to D.T.D. 363A and binary alloys containing over 7% magnesium, are difficult to cast by this process. Otherwise, there are very few engineering aluminium-base alloys which cannot be continuously cast.

When the work mentioned by Mr. Baker § was in progress the magnitude of the internal stresses in a continuous-cast ingot, 4½ in. dia., in Hiduminium R.R. 59 was estimated, and it was found that the sum of the hoop and longitudinal stresses on the outside skin of the billet was of the order of 21 tons/in.² (compressive), while in the centre it was about 10.5 tons/in.² (tensile). In order to determine the shape of the isotherms, a 16-in.-dia. billet was cast in Hiduminium R.R. 56, chosen because it does not normally crack in continuous casting. Temperature readings were taken at intervals by allowing a series of thermocouples, immersed in the metal, to descend with the billet. After plotting the isotherms which are shown in Fig. 2 of the article,§ it was found that there was a very steep temperature gradient between the outside and centre of the ingot, especially at points between 12 and 18 in. below the die.

* Chief Research Metallurgist, High Duty Alloys, Ltd., Slough, Bucks.

† J. M. Péloutier, *Rev. Aluminium*, 1947, (131), 84.

‡ J. Bingel, *Arch. Metallkunde*, 1949, 3, (5), 174.

§ W. M. Doyle, *Metal Ind.*, 1945, 66, 370, 390.

In actual practice, this is approximately the distance below the die where cracking becomes audible when the casting conditions are not properly balanced. Minor modifications of the chemical composition of an alloy can eliminate some of the tendency to cracking. For example, the base composition of the alloy to D.T.D. 390, before the advent of continuous casting, contained up to 1.2% magnesium, which was necessary in order to ensure the minimum properties, especially in the case of strip. This particular composition was very prone to cracking during the continuous-casting process, but it was found that this could be eliminated when the magnesium was reduced to about 0.85%, without any sacrifice of the mechanical properties. Furthermore, the loss due to edge-cracking in the subsequent rolling operations was considerably lessened. In the light of experience, we do not favour any reduction in the cooling efficiency by using a longer die in order to eliminate cracking, because it is found that a longer die leads to a deterioration in quality. Our standard dies even for the largest ingots are only between 3 and 4 in. deep. A lowering of the casting temperature and a decrease in the speed are also helpful in reducing the magnitude of the residual stresses.

I should like to hear Dr. Scheuer's views on the subtle changes required in the subsequent thermal treatment of certain alloy rolling slabs necessitated by the introduction of continuous casting. For example, continuously-cast ingots in the binary aluminium alloy containing about 1% manganese, preheated in the normal way as for die-cast ingots before rolling, tend to produce sheet with a very large grain-size. However, when they are given a very lengthy reheating before rolling, so as to precipitate the manganese, subsequent grain growth during recrystallization is minimized. High-strength alloys, like those to D.T.D. 683, have a tendency towards a peripheral weakness due to coarse segregates, below the level of the metal removed by the normal machining or scalping operation. A reduction of the speed of casting and the use of an improved design of baffle which distributes the liquid metal more efficiently in the die, brings this phenomenon nearer to the surface. However, this class of alloy requires a deeper scalping operation than any of the other commercial aluminium alloys.

I agree with Dr. Scheuer that the roller strip-casting machine has a definite future, in the very limited application of the product from such a machine, once the engineering difficulties can be overcome.

DR. V. KONDIC,* B.Sc. (Member): On reading the paper one might think that what Dr. Scheuer calls the "conventional method" of ingot casting has had its day and would before long be of historical interest only. Against this, I should like to look at the problem of when to cast ingots by conventional and when by continuous methods as an example of dynamic equilibrium. When one or other metallurgical, engineering, or production variable becomes of major importance, the equilibrium shifts towards one or other field. In other words, I prefer to look on these casting methods in certain spheres of application as complementary rather than completely exclusive. Whilst there are cases and conditions in which the choice of the casting method is clear-cut, there are intermediate cases where the choice can be made only after very careful consideration. To illustrate this point one has only to look at Figs. 10 (b) and 16 of the paper. The shape of the solidification front can be made very much alike in the two cases. Thus, from the point of view of soundness and structure of an ingot, which are largely controlled by the progress of solidification, there is a range of ingot casting where there is little to choose between the two methods. The question whether a faster rate of cooling, or

* Lecturer in Industrial Metallurgy, Birmingham University.

some other metallurgical or production factor, may favour either method can only be decided for each particular and individual casting problem. Incidentally, the schematic representation of the solidification front in Fig. 16 is incorrect, as a certain amount of solidification takes place within the mould itself. This figure would have been clearer if both "all solid" and "all liquid" solidification fronts were indicated.

Finally, the implication that all machines embodying the continuous-casting principle involve a large expenditure appears to me to be over-emphasized. There are machines available the capital costs of which are not greater than those involved in purchasing conventional ingot moulds. In other words, the capital-cost problem in deciding whether to use continuous-casting methods is not really fundamental: casting machines could be made at competitive prices, and the ultimate solution of the problem depends on consideration of overall factors.

MR. J. THEXTON,* A. Met., A.I.M. (Member): Dr. Scheuer refers to the considerable efforts being made to apply continuous casting, particularly those methods using a vertical mould open at both ends, to the higher-melting-point metals and alloys. I am interested in the continuous casting of both ferrous and non-ferrous alloys with melting points above 1300°C . and with casting temperatures of 1450°C . or over, and would like to add a few observations on the solidification of these high-melting-point alloys in a continuous-casting machine. I shall consider the solidification process in relation to the last three conditions of Dr. Scheuer's ideal casting process, namely, rapid heat extraction, directional solidification, and the production of a plane solidification front.

Rapid heat extraction in the initial stages is a prerequisite to the majority of continuous-casting processes and is effected by the use of a water-cooled mould. As Dr. Scheuer has said, this extraction of heat is controlled by the temperature gradient between ingot and mould, the thermal conductivity of the mould walls, and the degree of contact between the metal and the mould. In the case of the higher-melting-point alloys, such as steel and nickel-base alloys, the amount of heat to be extracted is so much greater than with the light alloys that the most efficient mould conditions must be used. Some idea of the amount can be obtained by considering their total heat/unit volume. Simple calculations with iron, nickel, and aluminium show that the values of the total heat/unit volume from 100°C . above the melting point to room temperature are 2700, 2400, and 700 cal./c.c., respectively. This fact was appreciated some 20 years ago by E. R. Williams, who developed a thin-walled copper mould around which water was circulated at a high velocity. This is the most successful type of mould developed for the continuous casting of steel, and is used in those machines successfully in operation in the U.S.A. at the present time. It is stated that after about 30 sec. the thickness of the outer shell of steel is 2 cm.

The rapid extraction of heat from the high-melting-point alloys during the early stages of casting, therefore, presents no real difficulty, and when the rate of heat extraction by the mould suddenly falls as a result of billet contraction, so that contact between billet and mould is broken, the outer skin on the billet is then strong enough to withstand the best cooling conditions, that is, the direct impingement of water on the solidifying billet.

The stage has now been reached in the solidification process where concern is with the extraction of heat from the central portion of the billet, the controlling factor in which is the thermal diffusivity of the alloy being cast. The high thermal diffusivities of aluminium and its alloys (0.5-0.7 C.G.S.

* Research Metallurgist, Development and Research Department, The Mond Nickel Co., Ltd., Birmingham.

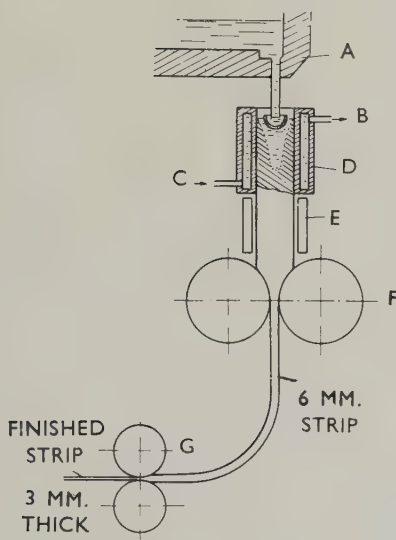


FIG. A.—Diagram of Combined Casting-Rolling Equipment. (*Brenner.*)

KEY.

- | | |
|--------------------------|----------------|
| A. Holding furnace. | E. Insulation. |
| B. Cooling-water outlet. | F. Hot rolls. |
| C. Cooling-water inlet. | G. Cold rolls. |
| D. Mould. | |



FIG. B.—Showing Reduction of 4 in.-dia. Billet to $\frac{3}{8}$ -in.-thick strip. (*Brenner.*)

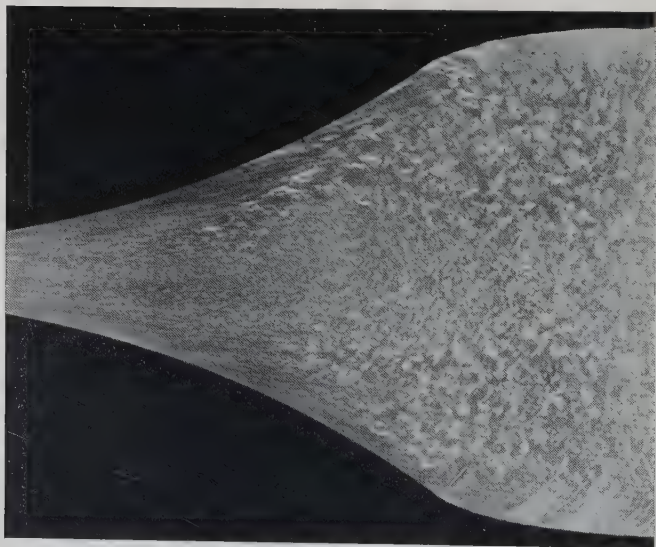


FIG. C.—Photomicrograph of Longitudinal Section of Strip. (*Brenner.*)

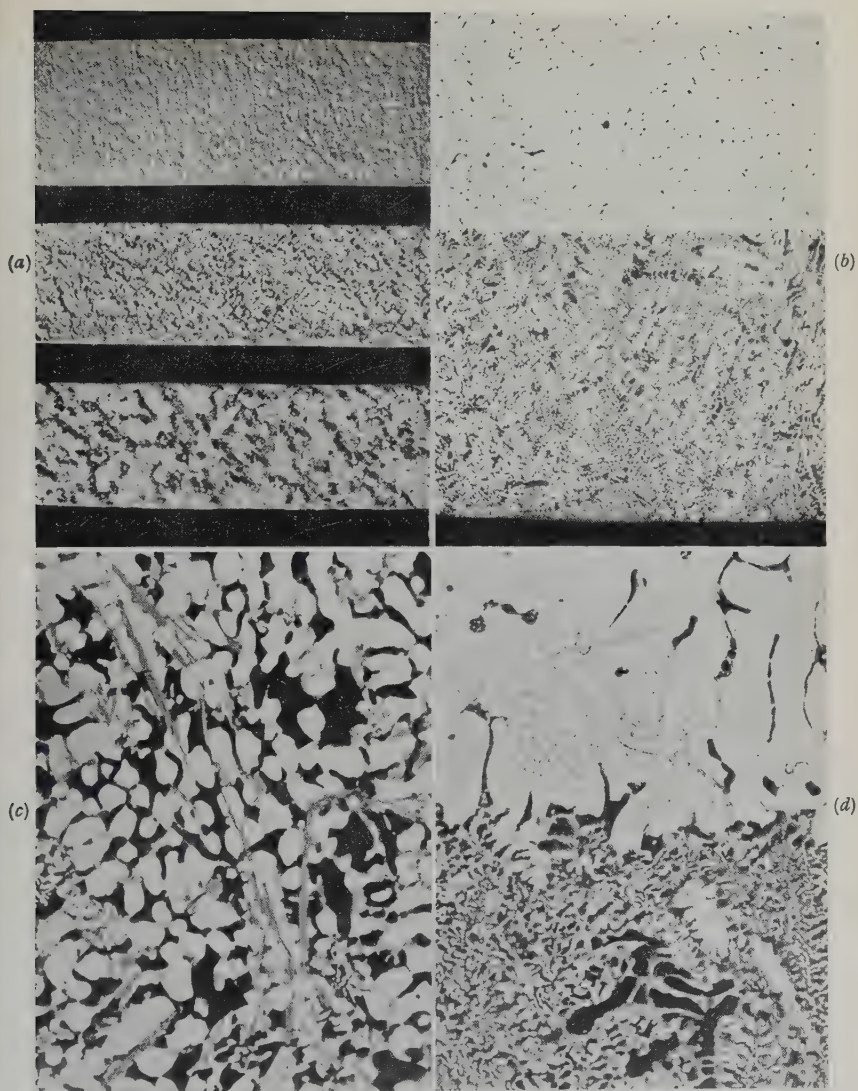


FIG. D.—Segregation in Continuously-Cast Avional Billet. (*v. Zeerleder.*)

(a) Eutectic exudation on surface. $\times 1$.

(b) Eutectic exudation on edges of bar. $\times 30$.

(c) Exudation of ternary eutectic of $\text{Al} + \text{CuAl}_2 + \text{MnCuAl}$ compound. $\times 300$.

(d) Eutectic exudation showing manganese enrichment at transition zone. $\times 150$.

All reduced by $\frac{1}{4}$ in reproduction.

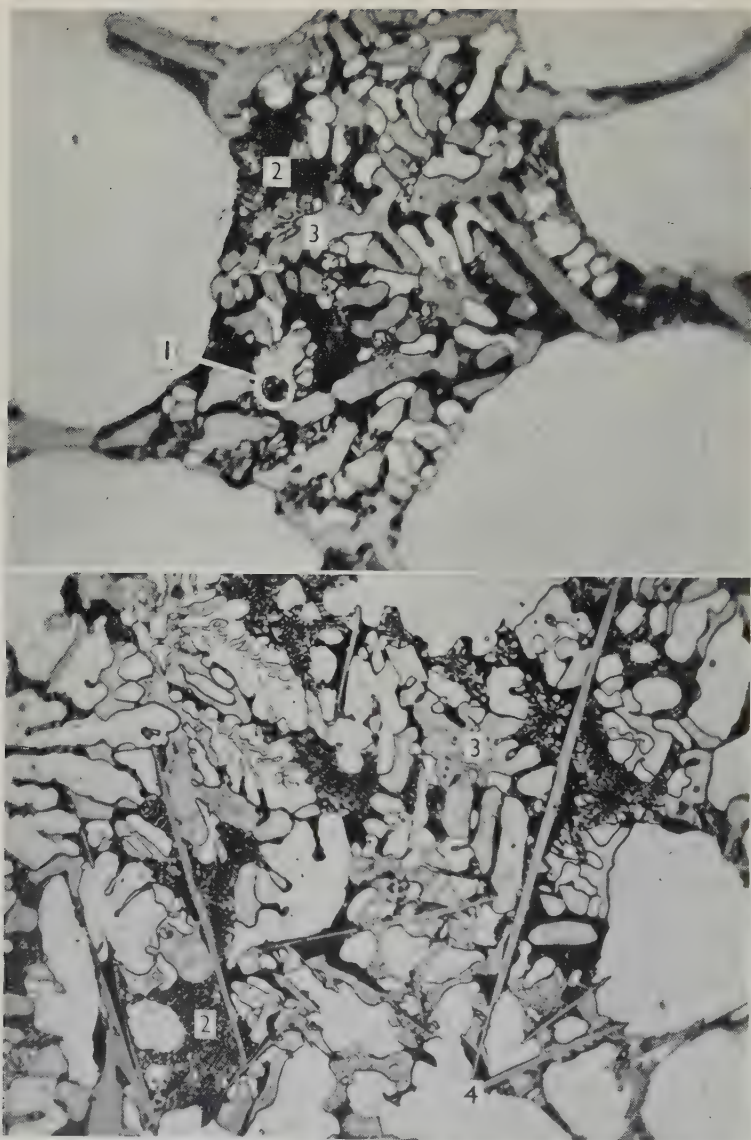


FIG. E.—Structure of Segregate at Crack in Continuously-Cast Avional. Etched in HF and HNO_3 . $\times 500$. (v. Zeerleder.)

1. $\text{Al} + \text{Mg}_2\text{Si}$.
2. $\text{Al} + \text{Al}_2\text{Cu} + \text{Mg}_2\text{Si}$ eutectic.
3. Al_2Cu .
4. Al-Fe-Cu needles.

units) result in quick transfer of heat from the centre to the outside of the billet and consequently quick solidification of the whole billet. Because of the high thermal diffusivities, the solid billet exerts a profound cooling effect upon the molten metal above and a large amount of heat is extracted longitudinally, i.e. directional solidification occurs. A further result is that during the radial extraction of heat in the mould, the rate of heat flow from the centre of the billet will be so high that a shallow solidification front will be produced. The ideal of a plane solidification front is approached as a result of the longitudinal cooling already mentioned.

In the case of steels and nickel-base alloys, however, a very different picture presents itself. Their thermal diffusivities, both above the liquidus and below the solidus, are only of the order of 0.04-0.05 C.G.S. units, that is, one-tenth to one-twentieth of the values for light alloys. This will have a profound effect upon the type of solidification. Extraction of heat will be almost entirely radial and directional solidification will not occur. The orientation of the crystals in the final billet will thus be the same as in ingots cast by conventional methods, although it is to be expected that the accelerated radial cooling will produce a finer grain. Moreover, since the heat is moving out radially and the thermal properties are poor, the solidification front will be V-shaped and very far from the ideal plane front. During the continuous casting of steel by the vertical-mould process, the V solidification front is, in fact, some feet in depth.

From this consideration of the mechanism of cooling of steel and nickel-base alloys in the open-ended vertical-mould-type machine, it is clear that while this process nearly approaches the ideal casting process, and hence the ideal billet, with light alloys, it is very far from the ideal in the case of the high-melting-point alloys. The ideal, of course, if attainable would be completely uneconomical. For example, in the hypothetical case of a steel ingot, 6 in. long, cooling from 1550° C., heat being extracted only from the bottom face which is at 0° C., it would take over 45 hr. for the whole of the ingot to cool 200° C. to 1350° C.

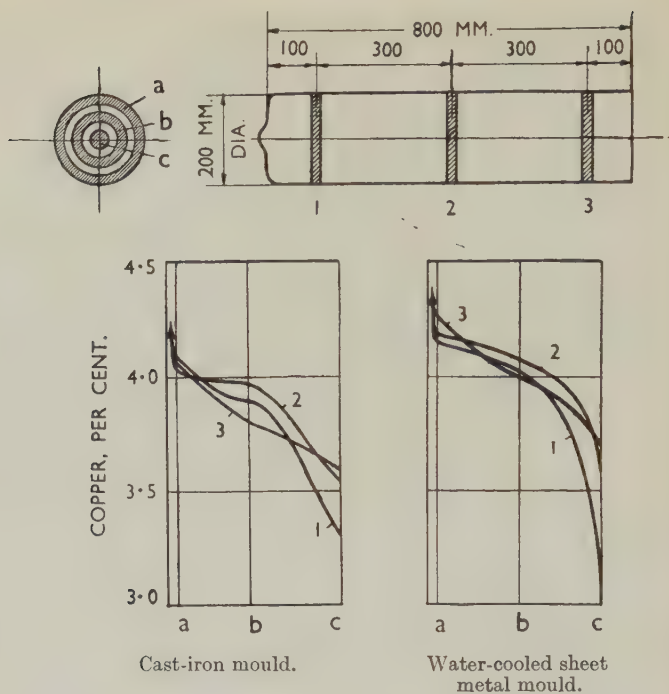
The presence of a deep solidification front in the billet during casting is not a serious matter, provided there is an adequate supply of molten metal with sufficient superheat to provide a continuous feed. It must be accepted that the final billet will show some measure of pipe at the end and that this unsound portion must be cropped off before the billet is processed. In spite of the lower yield of a steel or nickel alloy billet, as compared with a light alloy billet, the continuously-cast billets will show a much improved yield over those cast by conventional methods.

PROFESSOR DR.-ING. A. VON ZEERLEDER* (Honorary Corresponding Member to the Council for Switzerland): Inverse segregation, which causes a great deal of trouble in the production of aluminium alloys, is unfortunately sometimes on a much greater scale than indicated by Dr. Scheuer. As shown in Fig. D (Plate CIV) in continuously-cast Avional billets of 400 mm. dia. we have sometimes encountered a surface segregate possibly 2 mm. thick, with the following eutectic compositions:

Al + Al ₂ Cu + Cu ₂ Mg ₂ Al ₅	with 27% copper
Al + Al ₂ Cu	„ 33% „
Al + Al ₂ Cu + Mg ₂ Si	„ 28% „
Al + Al ₂ Cu + AlCuMn	„ 31.5% „

Fig. E (Plate CV) gives photomicrographic detail of the structure of the segregate at a crack in continuously-cast Avional. Fig. F shows diagram-

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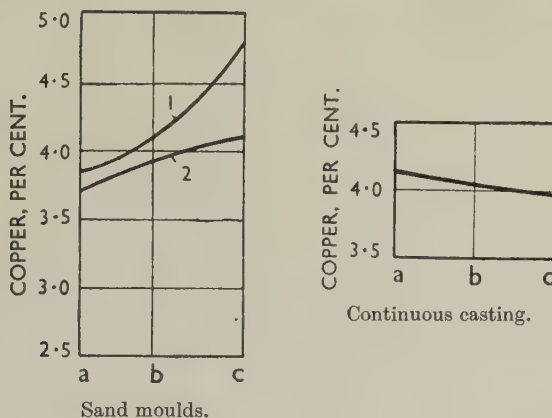


%	a	b	c	a	b	c
	Zone 1.			Zone 1.		
Cu . . .	4.10	3.89	3.30	4.14	4.03	3.05
Mn . . .	0.50	0.50	0.48	0.46
Mg . . .	0.52	0.49	0.46	0.42
Si . . .	0.18	0.27	0.23
Fe . . .	0.29	0.29	0.25
	Zone 2.			Zone 2.		
Cu . . .	4.04	3.98	3.56	4.18	4.08	3.53
Mn . . .	0.51	0.51	0.49	0.49
Mg . . .	0.52	0.50	0.46	0.44
Si . . .	0.27	0.24	0.23	0.40
Fe . . .	0.30	0.29	0.24	0.27
	Zone 3.			Zone 3.		
Cu . . .	4.06	3.82	3.58	4.25	4.02	3.72
Mn . . .	0.50	0.50	0.50	0.49
Mg . . .	0.55	0.53	0.51	0.46
Si . . .	0.28	0.25	0.24	0.42
Fe . . .	0.28	0.26	0.23	0.30

FIG. F.—See opposite page for legend.

matically the amount of segregation occurring in Avional bars cast by various methods.

Vosskühler recently published an interesting paper* on segregation in aluminium-copper-magnesium alloys, in the form of semi-continuously-cast flat rolling slabs of 152 mm. thickness (see Fig. G). In this he showed that segregation is a much more complex process than has hitherto been supposed.



%	a	b	c	a	b	c
Zone 1.						
Cu . .	3.84	4.11	4.84	4.14	4.05	3.98
Mn . .	0.49	0.49	0.52	0.55	0.54	0.54
Mg . .	0.50	0.48	0.54	0.49	0.48	0.48
Si . .	0.35	0.35	0.43	0.35	0.33	0.32
Fe . .	0.27	0.29	0.36	0.32	0.29	0.28
Zone 2.						
Cu . .	3.71	3.94	4.13			
Mn . .	0.49	0.50	0.50			
Mg . .	0.47	0.48	0.48			
Si . .	0.36	0.35	0.39			
Fe . .	0.26	0.30	0.29			

FIG. F.—Segregation in Avional Bars with Various Methods of Casting. (v. Zeerleder.)

Our observations at the Neuhausen laboratories, studying semi-continuously-cast round extrusion billets (see Fig. H), largely confirm Vosskühler's findings.

The AUTHOR (*in reply*): Regarding Mr. Baker's remarks on the continuous casting of copper alloys, I doubt whether it is true that copper alloys can only be cast in reciprocating moulds. I have seen copper cast in stationary moulds, and I do not think that there is any fundamental difference in this respect between aluminium and copper or copper alloys.

I am not quite clear about Mr. Baker's second question. The reduction of internal stress in cooling by keeping the lower part of the billet hot is, in

* Z. Metallkunde, 1949, 40, 305.

principle, equivalent to a stress-relief annealing process. Of course, if it means reducing the temperature gradient in the solidification zone, it would defeat—at least in part—the object of the continuous-casting process, and if it means reheating only the lower part of the billet without interfering with the temperature gradients in the solidification zone, it would not affect the stresses leading to the formation of hot tears in that zone.

Dr. Doyle mentions an interesting case of reducing the danger of hot tears by the alteration of the composition of the alloy, which can be considered as the effect of changing the mode of solidification.

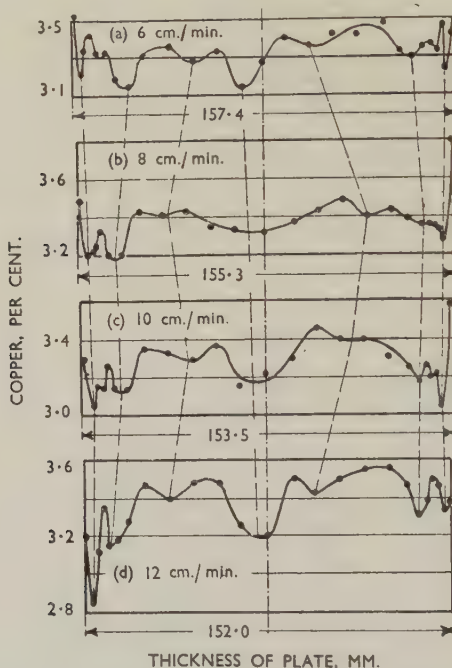


FIG. G.—Copper Segregation in Semi-Continuously-Cast Al-Cu-Mg Alloy Rolling Slabs Quenched at Various Speeds. (*Vosskühler*, cited by *v. Zeerleder*.)

The interesting statement by Mr. Thexton regarding heat extraction from high-melting-point alloys seems to show that these alloys are either much less inclined to develop hot tears than the high-strength aluminium alloys, or else that the hot tears heal in the subsequent extrusion or forging operations. It would be interesting if Mr. Thexton could state which of these alternatives is the correct one.

Professor von Zeerleder's communication regarding inverse segregation in billets produced by the continuous-casting process should be considered under two headings: (i) the production of exudations on the surface of the billet, and (ii) segregation in the interior of the billet. Exudations can be a mainly superficial phenomenon which does not necessarily prove that there is at the same time considerable segregation in the interior. With reference to the very com-

plicated pattern of segregation which Professor von Zeerleder and others have found in the interior of the billets, I would like to mention that there are, in billets cast with a reduced amount of chilling, zones of different crystal size and shape arranged roughly but not consistently parallel to the sides of the billet (the deviation from parallelism being caused by fluctuations in the pouring speed and perhaps the cooling-water supply). It may well be that the

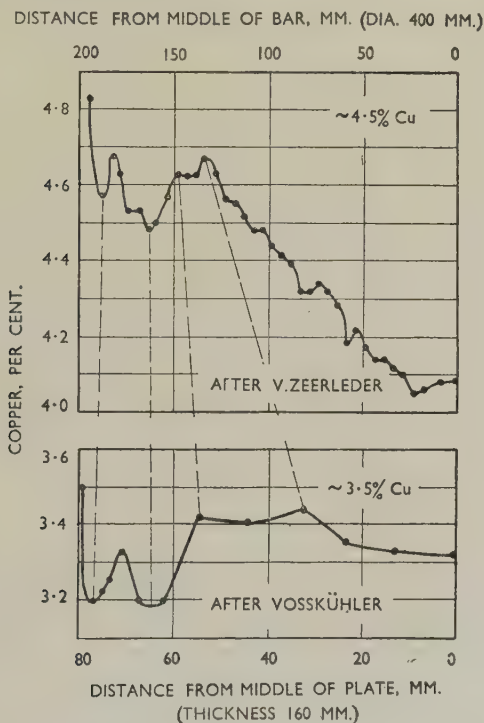


FIG. H.—Copper Segregation in Al-Cu-Mg Alloy Semi-Continuously-Cast Extrusion Billets. (*v. Zeerleder.*)

various maxima and minima on the graph of copper content in the billets described by Professor von Zeerleder can be connected with this zonal structure.

Dr. Brenner's measurements of coring by micro-hardness tests confirm what may be expected from theoretical considerations, viz. that the rapid chilling of the continuous-casting process does not produce a greater amount of homogenization in the cast structure, but creates conditions favouring rapid homogenization during the soaking period prior to rolling or forging.

Dr. Brenner's report on the rolling equipment combined with a continuous-casting plant of the sleeve-mould type, indicates that there are still developments in progress which are trying to give effect, in some other and perhaps more practical way, to Bessemer's idea of the combined casting and rolling process.

DISCUSSION ON THE PAPER BY DR. R. W. CAHN: "RECRYSTALLIZATION OF SINGLE CRYSTALS AFTER PLASTIC BENDING."

(*J. Inst. Metals*, this vol., p. 121.)

DR. K. W. ANDREWS,* B.Sc., A.I.M. (Member): Dr. Cahn has provided some very interesting experimental results and conclusions. It is of further interest to see that the effects described have not only been obtained with metals but also with rock salt, and possibly other inorganic crystals.

We have observed similar effects in quartzite pebbles (examined in connection with refractory investigations). A method, essentially the same as the Laue method, but using the mixed white and characteristic radiation from a copper or cobalt target, has been employed to estimate the crystal-size of these materials. In certain cases the pattern suggests two or three large crystals internally broken up into grains of slightly differing orientation. In one case, what was probably a single crystal appears to have been fragmented in this way, although the orientations of the fragments are randomly distributed about the mean (Fig. A, Plate CVI). In other cases (Figs. C and E, Plate CVI) the appearance of the asterisms suggests that there has been a breakdown into fragments whose orientations are produced in a more orderly fashion and are related to some specific direction in which the original crystal had been bent. Although the presence of more than one original grain makes the pictures more confusing, it is evident that the asterisms are very similar to some of those in Dr. Cahn's paper.

Back-reflection photographs are shown in Figs. B, D, and F (Plate CVI), corresponding, respectively, to Figs. A, C, and E. These photographs show similar effects and may also assist in the interpretation of the phenomena. Other back-reflection photographs (not illustrated) give evidence that in certain cases the quartz crystals are actually still in a condition of unrelieved strain.

In view of the nature of the radiation used, some of the darker spots within a single asterism will have originated from the characteristic components, but not all can be so accounted for. It therefore appears probable that the small crystallites are not disoriented in equal steps.

When an attempt is made to suggest how the breakdown into fragments has occurred, it is doubtful whether the phenomenon can be explained in terms of the movement of dislocations. The actual temperature at which the fragmentation took place may have been high enough for the new grains to have become mutually accommodated. This temperature, and in general the previous history of the quartzites, are not known. It does not, however, seem likely that a structure such as that of quartz could possess any mobile lattice defects, resembling dislocations in metals, even perhaps at high temperatures. On the other hand, one may suppose that the boundaries of fragments of slightly differing orientations would nevertheless be built up in some manner analogous to the simpler picture suggested for a metal, where a succession of edge dislocations of the same sign accounts for the boundary. It might even be more correct to suggest that in this case we are dealing with a less orderly phenomenon, and that the fragments are separated from each

* Research and Development Department, The United Steel Companies, Ltd., Stocksbridge, nr. Sheffield.

other in much the same way as the grains of an ordinary aggregate, except for the similarity in orientation. It would be interesting to have Dr. Cahn's opinion about this.

DR. A. F. BROWN,* : It seems a pity to raise a quibble on Dr. Cahn's excellent paper, but his explanation of how sufficient dislocations may be bunched together on one slip plane is not possible: if one inserts numerical values in the equation at the end of the paper it is found that the number per bunch must be about ten, whereas the number of active glide planes in each family corresponding to the strains given is about three or four.

The idea that dislocations may occur in clumps in a polygon boundary is, however, a valuable one and may help to explain the observed differences in etching behaviour between polygon boundaries and grain boundaries which one may picture as a continuous distribution of dislocations.

MR. R. W. K. HONEYCOMBE,* M.Sc. (Member) : I would like to confirm Dr. Cahn's result that polygonization can be obtained in hexagonal metals only after plastic bending and not after deformation in tension. An interesting feature of the tensile deformation of single crystals of hexagonal metals, in particular, is that if it is carried out carefully enough, no asterism results in X-ray Laue photographs even after 100% extension (Fig. G, Plate CVII). Glide is thus unaccompanied by bending of the lattice on either a macro- or microscopic scale, which would result in asterisms. If the extended crystals are bent, then asterism due to the macroscopic curvature of the lattice results. I have found that if cadmium crystals deformed in this manner are annealed, very striking polygonization results (Fig. H, Plate CVII). Prolonged annealing at high temperatures leads to coarsening, although this process is not as rapid as normal grain coarsening because of the slight orientation differences between the grains.

It has been shown by French workers † that in the case of aluminium, plastic bending is not necessary for polygonization to occur. Single crystals of aluminium, deformed a few per cent. in tension, polygonize when heated to a high temperature. I have carried out experiments with aluminium similar to those described above for cadmium and have found it impossible to avoid asterism in X-ray photographs from specimens deformed a few per cent. in tension. It should be mentioned in this connection that Burgers and Lebbink ‡ still obtained asterism in aluminium crystals deformed by shear along the glide plane in the glide direction. The interesting and crucial point of the matter is that I have usually observed intensity maxima in the asterisms from the *as-deformed* crystals at low deformations. Experiments showed that this fragmentation of the asterisms was *not* caused by polygonization but occurred immediately on deformation at room temperature. This suggests that aluminium crystals, even when deformed small amounts at room temperature, fragment, or that the lattice degenerates into a series of blocks differing slightly in orientation and connected probably by bent regions. The blocks could cause the intensity maxima, while the bent regions would contribute to the background of the asterisms. This fragmentation, if it can be thus designated, should not be confused with the fragmentation described by Wood § who believes that fragments about 10^{-4} – 10^{-6} cm. in size are present in severely worked polycrystals. The blocks to which I refer, about 0.05 mm. in width in 99.5% aluminium, occur in the very early stages of deformation.

* Cavendish Laboratory, Cambridge.

† A. Guinier and J. Tennevin, *Compt. rend.*, 1948, **226**, 1530.

‡ W. G. Burgers and P. J. Lebbink, *Rec. Trav. Chim.*, 1945, **64**, 321.

§ See, for example, W. A. Wood and W. A. Rachinger, *J. Inst. Metals*, 1948–49, **75**, 571.

Positive evidence of their existence is obtained by microscopic examination of electropolished aluminium single crystals which have been deformed by 5–10% elongation. In oblique illumination, fine bands less than 0.01 mm. wide and 0.05 mm. apart have been observed to occur uniformly throughout all crystals examined. Further investigation has shown that these bands are regions where the lattice is sharply bent, i.e. they are kinks or deformation bands joining relatively unbent regions of the lattice which differ slightly in orientation. The bands are particularly well shown up by an X-ray microscopic technique similar to that devised by Berg* and by Barrett.† Fig. I (Plate CVII) shows an X-ray reflection from an aluminium crystal deformed by 4%; the dark bands correspond to deformation bands produced in the crystal after this relatively small deformation. Recent work of my own has shown that these deformation bands almost always occur in aluminium single crystals deformed carefully in tension. I am of the opinion that they are directly responsible for much of the asterism observed in X-ray photographs from deformed crystals.

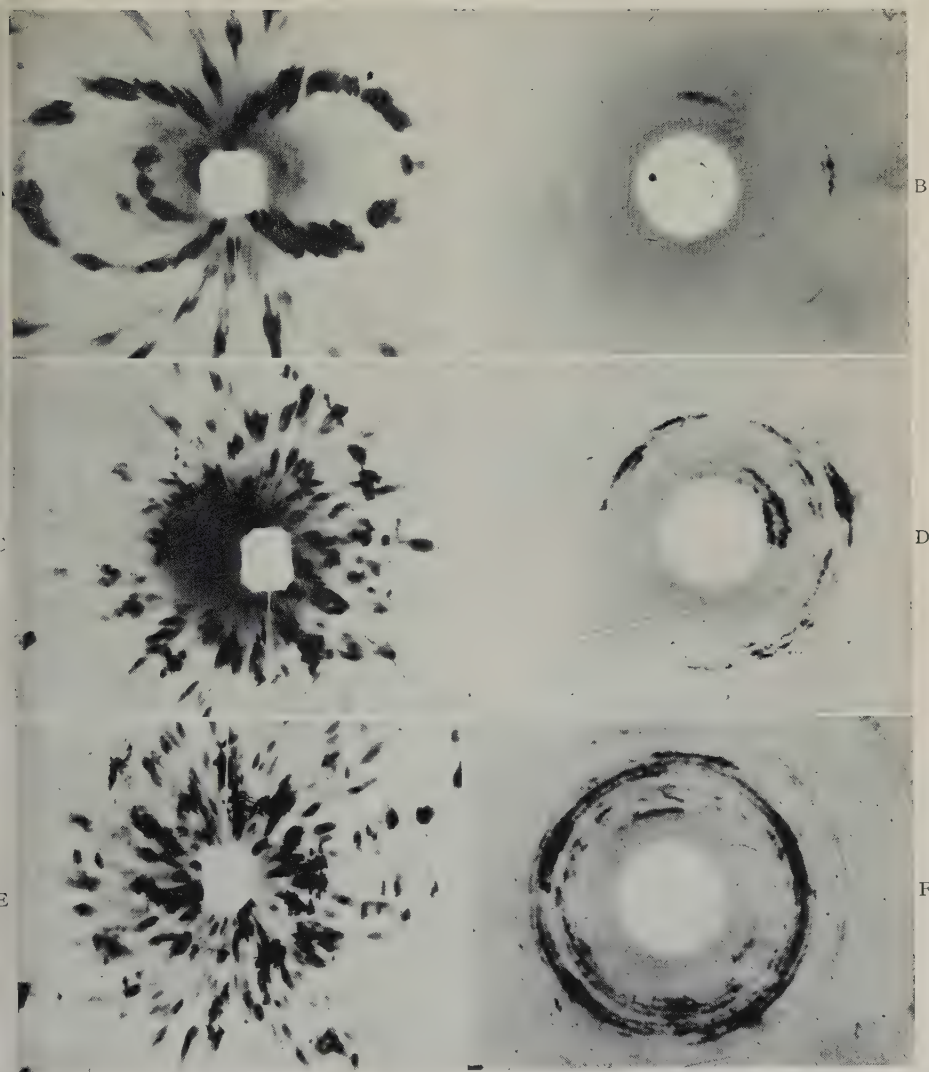
These results show clearly that the behaviour of hexagonal and cubic metal crystals on deformation by tension is quite different, and the difference is reflected in their behaviour on subsequent annealing. Cadmium deforms markedly without asterisms appearing in X-ray photographs and without the formation of deformation bands. Annealing results in no polygonization but in complete recovery, as was shown by Haase and Schmid‡ as early as 1925. On the other hand, aluminium shows fragmented asterisms in the very early stages of deformation and on annealing these asterisms fragment further (owing, of course, to polygonization). Complete recovery is not possible.

It is important to consider whether polygonization is to be identified generally with the mechanism of recovery or whether it is merely a phenomenon which occurs at elevated temperatures after most of the recovery has taken place. It must first be realized that the Laue method is relatively insensitive and a continuous asterism may result from a series of blocks very closely orientated to each other. The focusing X-ray method of Guinier and Tennevin§ does reveal polygonization in aluminium at temperatures as low as 300° C., at which stage Laue photographs still show continuous asterisms. This evidence would seem to support a polygonization theory of recovery. I have examined the recovery of deformed aluminium crystals by determination of change in yield point and by X-ray examination, and it is clear that the nature of the recovery curves is similar at all temperatures between 200° and 450° C. X-ray photographs show that polygonization is definitely occurring at 450° C. and we are left to infer, because of the similarity of the curves, that polygonization is also occurring at very much lower temperatures. Of course, the early stages of recovery may not result in the production of very definite walls of dislocations, but the migration of dislocations along the glide planes will have begun. In the case of hexagonal metal crystals, deformed only in tension, there is no evidence of polygonization and recovery is often complete. This seems to be against a polygonization theory of recovery, but if it is assumed that the diffusion of dislocations is not hindered by curvature of the lattice, then they are free to reach the surface of the crystal where they will produce a small step. It seems that in the case of cadmium deformed in tension, this diffusion of dislocations out of the crystal can occur and leave it almost completely recovered; whereas in a cubic metal, such as aluminium, this movement is hindered by the presence of the bent regions described above.

* W. Berg, *Z. Krist.*, 1934, **89**, 286.

† C. S. Barrett, *Trans. Amer. Inst. Min. Met. Eng.*, 1945, **161**, 15.

‡ O. Haase and E. Schmid, *Z. Physik*, 1925, **33**, 413. § *Loc. cit.*



Laue photographs.

Back-reflection photographs.

FIGS. A-F.—X-ray photographs of quartzite pebbles. Reduced by $\frac{1}{3}$ in reproduction. (Andrews.)

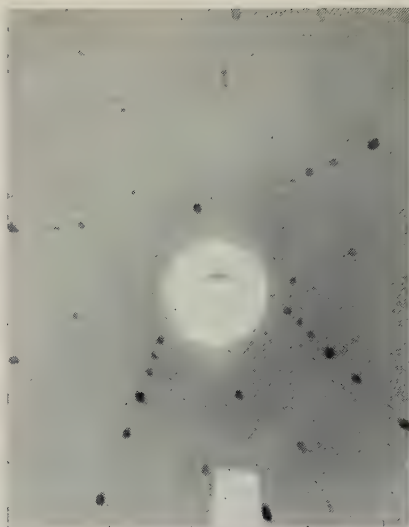


FIG. G.—Laue photograph of cadmium crystal after 100% elongation in tension. (*Honeycombe.*)

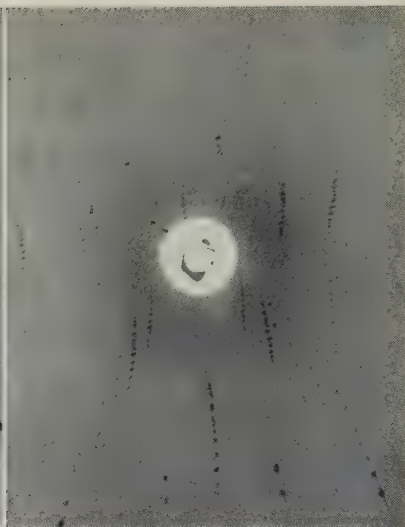


FIG. H.—Laue photograph of cadmium crystal deformed by 100% elongation, then bent to 7 mm. dia.; followed by annealing at 285° C. for 48 hr. (*Honeycombe.*)

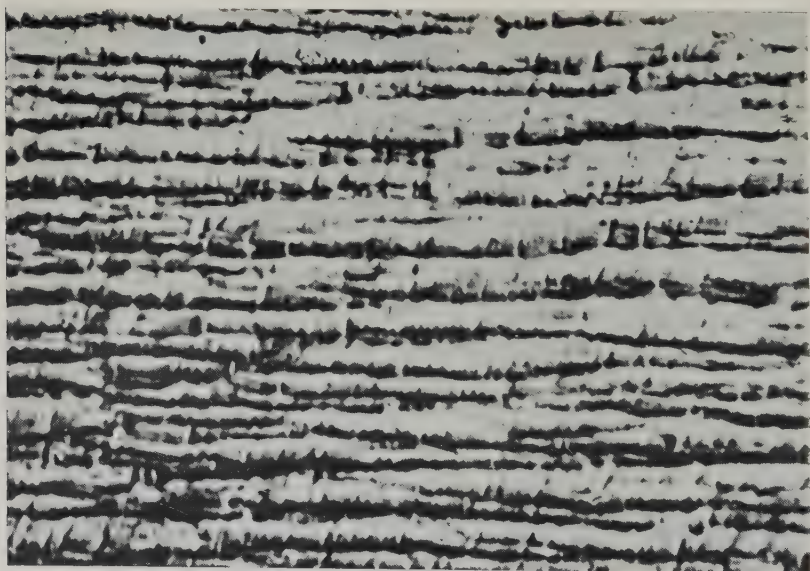


FIG. I.—X-ray micrograph of aluminium single crystal deformed by 4% extension in tension. $\times 50$. (*Honeycombe.*)

PROFESSOR H. O'NEILL,* D.Sc., M.Met., F.I.M. (Vice-President): Dr. Cahn mentions (p. 138) that the proposed mechanism of polygonization involves the accumulation of several dislocations on a "family" of glide planes. Reference is then made to the work of Heidenreich and Shockley, who showed that a glide plane or slip band consists of a family of associated and very closely spaced slip planes. It may be mentioned that this view of a slip band was proposed by Thompson and Millington,† twenty-five years ago, and was found acceptable by Rosenhain. The electron microscope will probably permit of its further elaboration, but hardness scratch tests and micro-indentation tests may also prove of value in obtaining further information.

In 1928 I‡ used scratch-hardness methods to explore the strain-hardening within a cold-worked single crystal of silicon ferrite, and noted the existence of certain peculiar "etch bands" within the strained portion of the crystal. Scratch tests revealed a progressive general hardening of the metal towards the region of maximum deformation, but it was also observed that the etch bands were regions of high local hardness. They might be compared with the "deformation bands" discussed on p. 140 of the present paper. Subsequent heating of the specimen produced alterations in the etching properties, and eventually some recrystallized grains were formed at the etch bands and were intimately associated with the latter. The new grains had a major axis in the same direction as that of the etch bands, and it was also reported at the time that "the straight boundaries noticeable in the new grains suggest that such boundaries are related to the traces of previous crystal slip". This observed straightness of the boundaries may correspond with the similar effect noticed in annealed zinc by Cahn, who comments on the stability of the new-grown structure when once it is formed. The scratch tests described indicated that the new grains had a higher hardness than that of the annealed unstrained metal, and it was suggested that these new crystals were still subjected to some hardening process. Perhaps this corresponds with imperfections and block structures in recrystallized grains, as described by Cahn on p. 123.

It is interesting to read on p. 135 that recrystallization probably occurs not at random but by a kind of recovery at the original lattice. This may be connected with an observation of my own§ that ball indentations in the recrystallized ferrite were surrounded by four lobes, as though the new aggregate had a preferred orientation. Finally, there is an unexplained ghostly marking running into a crystal boundary in Fig. 8 of my paper, which looks very much like what are to-day called dislocations in the Bragg bubble model of metallic crystals.

The AUTHOR (*in reply*): The etch bands to which Professor O'Neill refers were probably instances of the deformation bands referred to at the end of my paper (and with which Mr. Honeycombe deals in his discussion). If this is so, it is particularly interesting to know about the microhardness anomaly in the vicinity of the bands. The tendency for grains formed by recrystallization to grow preferentially into the bands and to be bounded by surfaces parallel to the bands also links with corresponding observations I have made recently with aluminium crystals. Professor O'Neill's data on the relative hardness of the new grains and of the original crystal are of great interest. They are not in agreement with the observation recorded in my paper (pp. 124 and 138) that grains formed by recrystallization of strained polycrystalline metal are themselves strained, but that those formed from strained single

* Professor of Metallurgy, University College, Swansea.

† *J. Iron Steel Inst.*, 1924, **109**, 67.

‡ *Trans. Amer. Inst. Min. Met. Eng., Iron Steel Div.*, 1928, 229.

§ *Loc. cit.*, p. 245.

crystals are perfect. The difference between the two cases will need further investigation.

The nature of *sub-grains*, in their numerous manifestations, has given rise to some almost heated debate recently, and I am therefore glad that Dr. Andrews, in his most interesting contribution, has himself suggested that the similarity between polygonization and the sub-grains he has found in quartzite may be a superficial one only. I agree with him that in the wholly homopolar lattice of quartz, dislocations could hardly move about very readily, and indeed no plasticity has ever been found in quartz, to my knowledge. It seems more probable that the sub-structure in the pebbles is an instance of lineage.* The quartz was presumably formed by growth from nuclei, either hydrothermally or from the melt, and growth might proceed as it does when, say, zinc or tin crystals are made from the melt, with a number of strips of slightly differing orientation separated by lineage boundaries. It is an interesting fact that lineage boundaries in aluminium crystals made from the melt etch up in exactly the same discontinuous way as polygon boundaries, though it would perhaps be rash to speculate on the reason.

I am grateful to Dr. Brown for pointing out the difficulty in connection with the concept of dislocation bunches. This becomes all the more puzzling when it is remembered that the polygon boundaries are very close together at first, and the difficulty does not arise at this stage because the dislocation density on each boundary is small; yet the polygon blocks go on growing for a time of their own free will, even though the dislocation density on the boundaries increases as a consequence. I can only suggest that any dislocations on the same atomic plane take up equilibrium positions, say, some hundreds of Ångströms apart, so that the attraction which pulls dislocations to the polygon boundary is balanced against their mutual repulsion.

I was very interested in Mr. Honeycombe's contribution. His observations on asterism in aluminium crystals are largely in line with the results of the experiments touched upon at the end of my paper and to be published *in extenso* soon; the only difference between us is in the spacing of the bands, which I found to be rather farther apart than Mr. Honeycombe does. I concur entirely with him that these bands are, in extended crystals, responsible for much of the asterism which has in the past been ascribed to other causes. The situation here is, of course, quite distinct from that obtaining with my *bent* crystals.

The difference between hexagonal and cubic metals described by Mr. Honeycombe appears to be of fundamental importance, and I think it is very important for the theory of plasticity that a sound explanation should be found. It is possible that we must look to the microscopic lamellar sub-structure discovered by Graf † for the explanation.

The problem of the relation between recovery and polygonization is an awkward one. That some of the recovery of physical properties is due to polygonization is undeniable, but it must be remembered that polygonization can occur only where the lattice is curved. Yet recovery occurs in cases where it is not, for instance in naphthalene deformed by pure shear.‡ I think that in these cases we get the diffusion of dislocations right out of a crystal, as suggested by Mr. Honeycombe. This mechanism has incidentally been discussed in quantitative detail by Kuhlmann, Masing, and Raffelsieper.§ In cubic metals, where deformation always seems to involve lattice curvature, polygonization must play an important part too, as Mr. Honeycombe states.

* M. J. Buerger, *Z. Krist.*, 1934, **89**, 193.

† L. Graf, *Z. Elektrochem.*, 1942, **48**, 181; *Z. Physik*, 1943, **121**, 73.

‡ A. Kochendörfer, *Z. Krist.*, 1937, **97**, 263.

§ D. Kuhlmann, G. Masing, and J. Raffelsieper, *Z. Metallkunde*, 1949, **40**, 241.

DISCUSSION ON THE PAPER BY PROFESSOR
E. A. OWEN AND MR. D. P. MORRIS :
" THE APPLICATION OF X-RAY METHODS
TO THE DETERMINATION OF PHASE
BOUNDARIES IN METALLURGICAL EQUI-
LIBRIUM DIAGRAMS."

(*J. Inst. Metals*, this vol., p. 145.)

PROFESSOR E. A. OWEN* : Our paper was written with the object of correcting the unfortunate, and we think, erroneous impression of the application of X-ray powder methods to the determination of equilibrium diagrams which has been created by the Oxford workers. They have published several papers on this subject during the past ten to fifteen years, and we have now felt called upon to offer a reply from the standpoint of the physicist who is attempting to apply X-ray methods to the investigation of metallurgical problems.

We wish to emphasize at the outset that our work has been concerned with the determination of *equilibrium* diagrams. Whilst perhaps at the moment such diagrams are not of very great value to the industrialist, we regard them as being of the utmost importance from the theoretical point of view, and we believe that very little progress can be made in the true understanding of alloy systems and of the many complicated phenomena encountered in practice until accurate and reliable data are available for the simpler cases of thermodynamic equilibrium. Our aim in the past has been to arrive at such data, by means of the X-ray powder method.

Our paper falls, broadly speaking, into three sections in which we (1) reply to the criticisms of the Oxford workers, (2) point out some possible dangers of the microscopic method, and (3) report data which point to the conclusion that equilibrium conditions are much more easily attained in powder rather than in lump specimens.

We should like to add the following remarks to the points covered in the paper. Firstly, Hume-Rothery and Reynolds † have considered in detail the question of the homogeneity of the ingots and have made suggestions that the uniformity of composition may be judged from the resolution or otherwise of various lines in the X-ray spectrum photographs. We find that the only satisfactory method of dealing with this problem is by measuring the lattice parameters of powders prepared from different portions of the ingot, and we prefer to use a *focusing* camera for lattice-parameter measurement because it has a higher resolving power than the spectrum camera. This has been referred to in several of our papers.

Secondly, Hume-Rothery and Raynor have ignored this work in dealing with contamination and change of composition of the filings during annealing. The production of a satisfactory ingot has been one of the most important parts of the investigations carried out at Bangor, and we believe that the

* Remarks made in introducing the paper for discussion at the Annual General Meeting of the Institute held in London, March 1950.

† *J. Inst. Metals*, 1937, 60, 303.

methods described in the paper both to test for this and the composition of the filings provide a satisfactory safeguard in all except extreme cases. It may be added that in very few or no cases has a disagreement between a phase

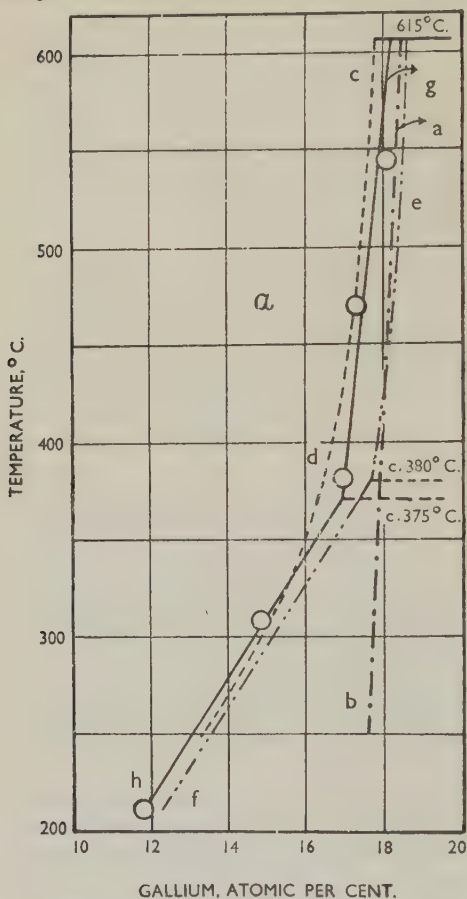


FIG. A.—Solubility of Gallium in Silver.

- ab* — Hume-Rothery, Mabbott, and Channel-Evans.
cd — Owen and Rowlands (original boundary).
ef — Hume-Rothery and Andrews.
gh — Owen and Rowlands (boundary adjusted by Owen and Morris).

boundary as determined by X-ray and microscopical methods been directly shown to be due to errors in the composition of the filings, and we believe that the possibility of contamination and change of composition has been much exaggerated. Furthermore, where such a disagreement exists (we except here errors due to decomposition on quenching) it is significant that newer microscopical investigations have on the whole tended to confirm the X-ray results rather than vice versa.

Thirdly, we should like to add another curve to Fig. 7 (p. 161) of our paper, as shown in Fig. A, taken from the paper by Hume-Rothery and Andrews* on the equilibrium diagram of the system silver-gallium, in which they criticize our work on the ground of length of time of annealing. Their results, as will be observed, corroborate very closely the original results of Owen and Rowlands. We wish to ask Hume-Rothery and Andrews how they reconcile this with the following statement from their paper: "At the lower temperatures, the present work shows that the solubility of gallium in silver diminishes more rapidly than had been indicated by any of the earlier investigations, and this is what would be expected. . . ."

In Section II of the paper we have advanced possible dangers of the microscopical method due to preparation of the specimens after heat-treatment. We have not ourselves obtained any instances of this, as we have confined ourselves mainly to pure X-ray work, but there are several statements in the literature which indicate that attention could profitably be paid to the effect of cold work and

* *J. Inst. Metals*, 1942, **68**, 133.

polishing on precipitation from supersaturated solid solutions and on the possibility of inducing phase transformations. The dangers we have visualized may, of course, be exaggerated, but it appears that definite experimental evidence on this point is required, and we should be glad to have the views of metallurgists in this connection.

As such transformations have been shown to be induced by plastic deformation in certain cases, we should also like to ask whether it is possible that the instances which have been given of decomposition on quenching could not have been produced, or if not produced accelerated, by the mechanical polishing of the specimen?

Finally, may we ask the metallurgists to explain: (1) how they ascertain that the surface of the specimen under microscopical examination is exactly in the same state and of the same composition as the interior of the specimen. (2) how they judge the state of equilibrium or how they can tell that the specimen under investigation is in true equilibrium?

DR. W. HUME-ROTHERY,* F.R.S. (Member): It is now eight years since the last discussion on the use of X-ray methods in the determination of phase boundaries in alloy systems took place at the Royal Institution.† At that meeting the general conclusion reached was that where the limits of a phase become more restricted with diminishing temperature, the X-ray method becomes increasingly attractive because microscopical examination may fail to detect very small precipitated particles. This point of view was expressed by Raynor and myself, and we also suggested that at the higher temperatures the advantage lay with the microscopical method, particularly because this often gave direct evidence of segregation or decomposition on quenching, which might lead to difficulties if X-ray methods were later employed. This view was not accepted by some of the X-ray physicists, but the general opinion of the meeting was that the two methods should be used in conjunction. Since then improvements have taken place in both the X-ray and the microscopical technique, and in particular, the long times of annealing required for the attainment of equilibrium at the lower temperatures have become increasingly apparent. On the X-ray side the work of the Bangor school has been outstanding, and it is unfortunate that this valuable X-ray work has led Owen and Morris to make an attack on the whole of the microscopical method and to support this by statements and diagrams some of which appear misleading as to the relative merits of the two techniques.

It would have been better if the discussion could have been confined to the experimental techniques, but the attack on the microscopical method is such that it should be answered. The authors' claims are extreme, particularly when they conclude that in determining an equilibrium diagram the main emphasis should be on the X-ray work, with microscopical examination used only as a secondary technique.

The authors have reached this conclusion mainly by presenting seven equilibrium diagrams of which two (copper-arsenic and silver-arsenic) were chosen "at random" from those they have examined. We may suggest that this is too small a number of diagrams to enable satisfactory conclusions to be drawn, but as the authors have used this method we shall consider first the diagrams which they have chosen.

Silver-Gallium.—The first investigation of this system was published in 1934 by Hume-Rothery, Mabbott, and Channel-Evans (H.-R., M., and C.-E.),‡

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† *J. Inst. Metals*, 1943, **69**, pp. 1-27.

‡ W. Hume-Rothery, G. W. Mabbott, and K. M. Channel-Evans, *Phil. Trans. Roy. Soc.*, 1934, [A], **233**, 1.

who with very restricted supplies of gallium were able to outline the liquidus, solidus, and solid-solubility curves. It must be emphasized that nothing would have been gained by using the X-ray method at this stage because the quantity of gallium available was too small to permit the precautions which Owen and Morris rightly say are necessary if the method is to be reliable. After admittedly inaccurate lattice-spacing work in 1936 by Weibke, Meisel, and Wiegels,* the lattice spacings and solid-solubility curve were determined in 1940 by Owen and Rowlands,† and in 1942 Hume-Rothery and Andrews ‡ described an independent investigation of the system, using microscopical methods at high temperatures and the lattice-spacing method at 211° C. The results of H.-R. and A. indicated a solubility at high temperatures approximately 1 at.-% greater than that of O. and R., and it was suggested § that this difference was the result of (a) longer periods of annealing, and (b) the fact that O. and R. used a straight-line lattice spacing/composition relation, whereas actually there was a slight curvature. In the paper now under discussion, Owen and Morris recalculate the data of O. and R. and remove some of this difference. Unfortunately in drawing their results to illustrate the relative merits of the two techniques, Owen and Morris compare the revised results with the H.-R., M., and C.-E. values of 1934, and not with the H.-R. and A. values of 1942. In this way the supposed advantage of the X-ray method is based on the assumption that the latest X-ray information of 1949 is to be compared with the earliest microscopical survey of 1934, to the complete omission of the microscopical work of 1942, in spite of the fact that it was this very work which led Owen and Morris to revise the results of Owen and Rowlands. The specimens of H.-R. and A. at the higher temperatures received longer periods of annealing than those of O. and R., and this may account for the slightly higher solubility indicated by the microscopical method. From Fig. 3 of the paper by O. and R., showing the lattice spacing/composition curve, it will be seen that at the higher concentrations there is room for a difference of several tenths per cent., so that it may reasonably be claimed that at present the two methods agree within their limits of accuracy.

In his introductory remarks, Professor Owen asked Hume-Rothery and Andrews how they justified the statement that their work showed the solubility of gallium in silver to diminish more rapidly than had been indicated by any of the earlier investigators. The answer to this question is that as compared with O. and R., H.-R. and A. obtained a higher solubility at high temperatures, and carried their determination down to 211° C., whereas O. and R. did not carry their work below 300° C. H.-R. and A. were thus the first workers to establish the solubility below 300° C., and if we understand Owen and Morris's paper correctly the lowest point shown on what they call the curve of Owen and Rowlands is really based on the lattice spacing given by H.-R. and A., and the slight differences in this region are presumably due to differences in the lattice spacing/composition curves of the two investigations.

Silver-Aluminium.—Fig. B was published by Hume-Rothery and Raynor in 1941,|| and compares the X-ray work of Foote and Jette ¶ with micro-

* F. Weibke, K. Meisel, and L. Wiegels, *Z. anorg. Chem.*, 1936, **226**, 201.

† E. A. Owen and V. W. Rowlands, *J. Inst. Metals*, 1940, **66**, 361.

‡ W. Hume-Rothery and K. W. Andrews, *J. Inst. Metals*, 1942, **68**, 133.

§ Owen and Morris are incorrect in saying that a dogmatic statement was made on this point.

|| W. Hume-Rothery and G. V. Raynor, *J. Sci. Instruments*, 1941, **18**, 74.

¶ F. Foote and E. R. Jette, *Trans. Amer. Inst. Min. Met. Eng.*, 1941, **143**, 151.

scopical work of Hume-Rothery, Raynor, Reynolds, and Packer.* Here the two methods were in quantitative agreement at the higher temperatures, although at the lower temperatures the microscopical work was in error owing to a failure to observe precipitated particles, this being the point emphasized

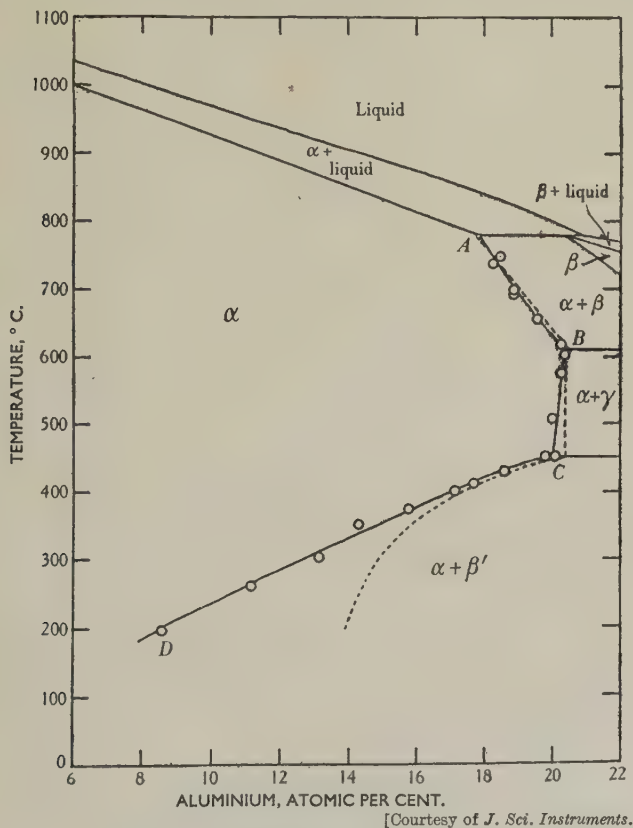


FIG. B.—Solubility of Aluminium in Silver.

— Foote and Jette.
 - - - Hume-Rothery, Raynor, Reynolds, and Packer.

by Hume-Rothery and Raynor at the 1942 discussion. Since then Owen and Morris have presented a diagram including previously unpublished work of Owen and Roberts which substantially confirms the work of Foote and Jette, although there are discrepancies which are of the same order as the difference between the microscopical and X-ray results at the higher temperatures. The position in this system is therefore just as it was in 1942, but in drawing their diagram Owen and Morris, although including the 1940

* W. Hume-Rothery, G. V. Raynor, P. W. Reynolds, and H. K. Packer, *J. Inst. Metals*, 1940, **66**, 209.

work of H.-R., R., R., and P. at low temperatures, where it was in error, have omitted it at the higher temperatures where it was accurate.

Silver-Arsenic.—For this system Owen and Morris compare the recent unpublished X-ray work of Owen and Roberts with the 1915 diagram of Heike and Leroux,* who examined only two alloys in the region of composition concerned, and gave these annealing treatments which were apparently† of only a few hours' duration. Owen and his collaborators are, of course, entitled to the fullest credit for the determination of the solubility curve, but it is clear that the relative merits of the two techniques are not to be tested by comparison between work of 1915 and of 1949.

Fig. 5 of the paper by Owen and Morris is of interest as indicating the reproducibility of the X-ray methods at the higher temperatures. This diagram shows that at the highest temperature the points obtained by Owen and Rowlands‡ and by Owen and Roberts differ by several tenths per cent., and the uncertainty of the maximum solubility at 595° C. is at least $\frac{1}{2}$ at.-%. This will be seen by drawing the most probable curves through the circles and the crosses in the figure, and the authors' estimate of ± 0.15 at.-% is clearly too small. The cause of this difference is difficult to see; it cannot be due to uncertainty in composition because the authors emphasize that they have not shirked the analysis of their filings. The volatility of arsenic should hasten the attainment of equilibrium, so that the difference is not likely to be due to lack of equilibrium in one determination. This diagram suggests therefore that even in the Bangor work, which is admittedly some of the most accurate in the world, the X-ray methods are not very precise at the higher temperatures.

Copper-Arsenic.—In this system the microscopical work of Hanson and Marryat,§ and of H.-R., M., and C.-E.,|| was in error, and this was almost certainly due to lack of sufficiently long annealing. This fact has been known since 1936, when the solubility was determined by the lattice-spacing work of Mertz and Mathewson.¶ According to these workers, the solubility of arsenic in copper decreases linearly from 7.9 wt.-% (6.78 at.-%) at 680° C. to 7.5 wt.-% (6.44 at.-%) at 300° C. Above 380° C., therefore, the results of Mertz and Mathewson, to which there is no reference in Owen and Morris's paper, agree very well with the curve in Fig. 4 of the latter paper. Below 380° C., however, there is marked divergence, amounting to 0.4 at.-% at 300° C. Both investigations appear to have been carried out with care, and the discrepancies do not support the contention of Owen and Morris that careful X-ray work leads to consistent results.

Copper-Indium.—In this system Owen and Morris quote unpublished work which agrees with that of H.-R., R., R., and P., at high temperatures, but at low temperatures gives a deviation opposite in direction from that usually found. Unfortunately, no experimental details are given, and until these are presented it is impossible to say which curve is more likely to be correct, although it may be noted that owing to an error in drawing, Fig. 6 of Owen and Morris's paper has slightly exaggerated the difference between the two investigations.

Aluminium-Zinc and Iron-Nickel.—These results will be discussed in detail

* W. Heike and A. Leroux, *Z. anorg. Chem.*, 1915, **92**, 119.

† The times of annealing of the alloys concerned are not stated, but those for other alloys in the system were of the order of a few hours.

‡ *Loc. cit.*

§ D. Hanson and C. B. Marryat, *J. Inst. Metals*, 1927, **37**, 121.

|| *Loc. cit.*

¶ J. C. Mertz and C. H. Mathewson, *Trans. Amer. Inst. Min. Met. Eng.*, 1937, **124**, 59.

by Professor Raynor, but it may be mentioned here that in the aluminium-zinc system Owen and Morris's diagram is misleading because it omits work from the Bangor school, which, although published only a year or two before that of Owen and Pickup, is now admitted to have been incorrect. As the authors have gone back 35 years to find faulty microscopical work in the system silver-arsenic, they should be impartial and go back one or two years when considering the X-ray work. It should also be pointed out that it is incorrect to claim, as has been done in Fig. 1, that Owen and Pickup closed the immiscibility loop in this system; as explained by Professor Raynor (p. 686), this was not done until later work by classical methods.

In the system iron-nickel, as Professor Raynor shows, the authors' diagram is misleading for the present purpose because it omits to point out differences between the results of Owen and Liu * and Owen and Sully,† and also does not state that quite different diagrams were produced by other X-ray workers of established reputation.

It will be seen therefore that when the authors' seven diagrams are carefully examined there is nothing to suggest that a change in the conclusions reached at the 1942 conference is now required. As emphasized above, the true comparison will only be reached by considering a larger number of diagrams, and for this purpose I have considered the whole of the work on the alloys of copper and silver which have been studied by X-ray methods at Bangor and of which I have personal experience in one way and another. In general there is, I am glad to say, very good agreement. Exceptions are shown in the systems copper-zinc and silver-zinc, where the X-ray work in the β -phase region is now generally recognized to have been much less accurate than earlier microscopical work owing to differences due to decomposition on quenching. Owen and Morris argue that this is not a defect of the X-ray method as such, but is simply an indication that a high-temperature camera should have been used. With this last conclusion we are, of course, in full agreement, but the statement is clearly inconsistent with Owen and Morris's earlier claim that their X-ray films indicate whether phases are in thermodynamic equilibrium. It is hardly reasonable to say in one part of the paper that the X-ray films indicate true equilibrium, and then to say later that if only the investigators had known that decomposition had occurred they would have used a high-temperature camera. Unfortunately, the authors go further than this and claim that "in general such systems are unsuitable for examination by *any* method employing quenched specimens, whether filings or lump material". This is quite incorrect, since the microscopical method is able to deal with decomposed specimens and to distinguish to a quite high degree of accuracy between alloys whose structures are of the (α + decomposed β) and wholly decomposed β types, respectively. The method fails only when the amount of α is so small as to be indistinguishable from the finely divided α in the "decomposed β ". This was stated explicitly at the discussion in 1942 by myself and Dr. Raynor, when photographs were shown of copper-gallium alloys to illustrate the point, and it was emphasized that by combining the X-ray and microscopical methods, the latter would often indicate that decomposition occurred and so give a warning which is clearly not always obtained from the X-ray films alone.

As stated, in the copper and silver diagrams there is, on the whole, very good agreement between the results obtained by the two techniques. In a few cases where the solubility diminishes at low temperatures the X-ray results have indicated a slightly smaller solubility and are probably to be preferred. In some other systems the maximum solubility determined by

* E. A. Owen and Y. H. Liu, *J. Iron Steel Inst.*, 1949, **163**, 132.

† E. A. Owen and A. H. Sully, *Phil. Mag.*, 1938, [vii], **27**, 614.

microscopical methods is slightly larger than that given by the X-ray technique, and here I think the microscopical results should be accepted, because they involve longer times of annealing and also refer to that part of the lattice-spacing/composition curve where the latter is least certain.

It will be seen, therefore, that this more comprehensive review of results obtained by the two methods serves only to emphasize that the conclusions reached in 1942 are substantially unchanged.

In introducing his paper Professor Owen asked what evidence there was that the specimens used in microscopical work had reached true equilibrium. The answer is that the method adopted is the same as that in the X-ray technique, namely, to anneal the specimens until further annealing produces no significant change. In this respect there is nothing to choose between the two methods, and it may be pointed out that in some of Professor Owen's work (e.g. on the system copper-arsenic) the lattice spacings were still altering slightly with further annealing, so that what Professor Owen really means is not that his specimens have reached true equilibrium, but rather that the changes have become so small that he thinks they may be ignored because they are of the same order as the accuracy of the lattice-spacing measurements.

Owen and Morris criticize the microscopical method very severely on the grounds that misleading results may arise from a strained condition of the surface, or from irregular etching effects. These difficulties have, of course, been recognized by metallographers for a very long time, but the argument that they should lead to a distrust of microscopical metallography in general is as unreasonable as it would be to suggest that the X-ray methods are unreliable because in some cases two phases give rise to diffraction spectra which are closely similar or have overlapping lines. Each method sometimes leads to confusing results, and it is for this reason that we have so strongly urged their use in conjunction with and not in isolation from each other. We may reasonably protest against the implication of Owen and Morris (p. 164) that equilibrium diagrams have been based on the microscopic examination of unetched alloys. The true position about the aluminium systems to which they refer is that the alloys concerned were, as a matter of routine, examined in the unetched state before being etched.* In some of the aluminium alloys it happens that relatively hard particles are seen in the unetched section, and these may possess characteristic shapes or colours which are naturally recorded before the specimens are etched. It will be realized, therefore, that there is no justification for the statement of Owen and Morris that "any attempt to infer the constitution and condition of the specimen by the microscopical examination of unetched polished surfaces is therefore likely to be misleading, although this seems to be fairly common practice for certain purposes".

We think we are also entitled to protest against the statement made on p. 149 of the paper to the effect that whereas the X-ray method provides a safeguard against contamination "no such tests are available in the microscopical method". This is quite untrue, since there are numerous statements in published papers that the actual specimens used for microscopical examination have been submitted to chemical analysis.

In their discussion of the relative times required for equilibrium to be attained in filings or in lump specimens, it is unfortunate that Owen and Morris made no reference to the general treatment of the problem by Hume-Rothery and Reynolds.† When an alloy is annealed, the establishment of equilibrium may require precipitation to occur from a particular phase, or,

* This is done to ensure that the surface is properly polished and to give evidence of any cracks or unsoundness.

† P. W. Reynolds and W. Hume-Rothery, *J. Inst. Metals*, 1937, 60, 365.

alternatively, the phase may have to take up one or more of the component metals into solid solution. If an alloy is homogenized,* quenched, and converted into filings and then re-annealed, the extreme deformation produced by the filing will generally result in processes of precipitation occurring more rapidly than when the quenched ingot is re-annealed, even though the latter has been severely deformed by hammering. If, on the other hand, the establishment of equilibrium requires a phase to take up one of the component metals into solid solution, the process will almost certainly be more rapid in a lump of the alloy than in the filings, unless a volatile metal is concerned. The filings of a polyphase alloy will contain some particles consisting of one phase alone, and it can hardly be suggested that reactions between the individual particles of a mass of filings occur more rapidly than between particles in the much closer contact which exists in a solid ingot. We suggest, therefore, that the conclusions of Owen and Morris that equilibrium is attained more rapidly in filings than in lumps is, except for volatile metals, the result of their having been concerned mainly with alloys in which precipitation occurs on re-annealing, and that the true position is as summarized above. It may be noted that, as shown in Section III, there are some cases where the microscopical work indicates a slightly higher *maximum* solubility than the X-ray method, and we suggest that this may be an illustration of the above principle.

We conclude, therefore, that everything is to be gained by combining the microscopical and X-ray methods. We have nothing but admiration for the Bangor work, but we suggest emphatically that no evidence has been produced which alters the general conclusions reached in 1942. If it is asked why the present authors have reached such different conclusions, it may be suggested that this is due partly to their having worked with alloys which are very suited to the X-ray technique, and partly because, at least so far as the work on copper and silver alloys is concerned, they have investigated systems in which the main form of the diagram had been laid out by previous work. Had they started these systems from the beginning, without any knowledge of the form of the diagram, they would probably have reached very different opinions as to the value of the microscopical method. Apart from the systems referred to above we have examined many others which have been investigated by both methods, and have found that each technique has its advantages and each has sometimes led to erroneous conclusions. The mistakes in the microscopical methods have usually been at the lower temperatures, as indicated in the discussion in 1942. At the higher temperatures the microscopical method is more simple and has dealt with alloys decomposing so quickly that the X-ray methods could succeed only by the use of high-temperature technique, which is difficult and, in some cases, impossible to apply owing to the reactivity of the alloys. We believe that little is to be gained by a broad discussion of the methods, but that each alloy system must be considered as a problem by itself. Some will be better examined by one method and some by the other, and in general the best results will be obtained by using the two methods together.

PROFESSOR G. V. RAYNOR,† M.A., D.Sc. (Member of Council): Dr. Hume-Rothery has made certain criticisms of this paper, in respect of several of the equilibrium diagrams discussed, and I now wish to refer to two more of the alloy systems.

* We use the term homogenization to include any preliminary annealing treatment which produces equilibrium at a high temperature, regardless of whether the equilibrium state is that of a single-phase or polyphase alloy.

† Professor of Metal Physics, University of Birmingham.

Aluminium-Zinc System.—In this case, the authors have hardly acknowledged sufficiently what the X-ray investigators owed, before starting work, to the previous classical researches, which dictated the methods adopted. It is true that the first hint that the β and γ areas in Fig. 1 of the paper really belonged to the same phase came from the X-ray workers,* but these workers did not determine the complete ($\beta + \gamma$) loop. We must not, however, lose sight of the fact that classical metallurgical methods were capable of getting the right answer too.

In Fig. 1 the authors reproduce Tanabe's diagram as an illustration of an incorrect piece of work, and Owen and Pickup's diagram as the correct one.† But they say nothing about the work of Owen and Iball,‡ who used high-temperature X-ray results to produce a phase diagram which was seriously wrong in several particulars. In order to avoid presenting a false idea of the reliability of X-ray work, these results should have been quoted. To quote briefly from Owen and Iball's paper, which was published during the year before the diagram shown in Fig. 1: "In the first place, the X-ray data suggest that this temperature [the transformation temperature, given as 272° C. in Fig. 1] lies between 300° and 310° C., which is higher than that previously recorded by any of the investigators of this system. At temperatures above 300° C. the extent of the γ phase is found to be much reduced, and what was previously regarded as pure γ phase has been shown to consist of a mixture of the two face-centred cubic structures with slightly different parameters." At 375° C., the two-phase region deduced was from 45% to about 98% aluminium. It is significant that the authors said: "The change in parameter of the γ phase is so small that the whole drop across the region of pure γ solid solution is almost within the range of experimental error. This makes it impossible with this method to fix a definite limit to the solubility of zinc in aluminium at this temperature, but it appears to be very small." It is clear that, had Owen and Iball's results been plotted together with Gayler and Sutherland's diagram,§ serious doubts would have been cast on the reliability of the X-ray method. I do not, of course, regard this as a fair comparison, but neither is Fig. 1 of the paper entirely fair. Comparison of the most recent work by both the X-ray and microscopic method shows reasonable agreement.

The diagram which Owen and Pickup produced was not quite that attributed to them in Fig. 1. The two limbs of the ($\beta + \gamma$) boundary did not quite join up. In their paper, Owen and Pickup say: "The present X-ray data do not confirm the existence of the ($\beta + \gamma$) region above about 360° C., but, if it exists, it covers a range of compositions much less than 1%". Later, in the same paper, we find: "in the present work it [the ($\beta + \gamma$) region] is found to extend over about 3% at 350° C. . . . above this temperature the ($\beta + \gamma$) region up to the peritectic line at 440° C. is, therefore, found to occupy an exceedingly narrow range of composition". At this date the X-ray workers seemed to be unable to say definitely whether a completely closed loop existed or not. Fink and Willey|| decided the question in 1936 as a result of electrical-conductivity work; as far as I know, their diagram was the first to show the two-phase region as a completely closed loop. As the authors say, this was confirmed in 1938 by Gayler and Sutherland.

I think that Fig. 1 of this paper gives a false impression unless the whole story of the development of this diagram is told.

* E. Schmid and G. Wassermann, *Z. Metallkunde*, 1934, 26, 146.

† E. A. Owen and L. Pickup, *Phil. Mag.*, 1935, [vii], 20, 761.

‡ E. A. Owen and J. Iball, *Phil. Mag.*, 1934, [vii], 17, 433.

§ M. L. V. Gayler and E. G. Sutherland, *J. Inst. Metals*, 1938, 63, 123.

|| W. L. Fink and L. A. Willey, *Trans. Amer. Inst. Min. Met. Eng.*, 1936, 122, 244.

Iron-Nickel System.—It is hardly correct to state that before the work of Owen and Sully numerous investigations had been made on the binary system iron-nickel. Much work had certainly been done, but on impure alloys which were really specimens of ternary or more complex systems; this was due to absence of pure materials rather than to carelessness on the part of the investigators. No full-scale micrographical examination appears to have been carried out on pure alloys and no direct comparison between the two techniques can be made. With reference to the reliability of X-ray methods, however, it should be pointed out that Owen and Morris fail to mention that X-ray investigators have produced quite different results for the lattice spacings and solubility limits in this system. In the work of Owen and Liu * this point was recognized, and the lattice-spacing method was discarded and replaced by that of vanishing phases, a point which the authors do not mention. This work showed that the $\alpha/(\alpha + \gamma)$ boundary at 300° C. given by Owen and Sully † was in error by about 3%. This clearly requires considerable modification of the claims of the authors that lattice-spacing methods indicate whether constituents have reached thermodynamic equilibrium. I also feel that Fig. 2 of the paper is misleading, in so far as it gives the impression that the X-ray work of Owen and Sully and of Owen and Liu agreed exactly for the $(\alpha + \gamma)/\gamma$ boundary. The figures tabulated in the two relevant papers do not, however, show such agreement (Table A).

TABLE A.

Temp., ° C.	Owen and Sully Nickel, at.-%	Owen and Liu Nickel, at.-%
800	4.5	3.8
700	9	9.4
600	14	17.3
550	18.5	22.2
500	26.5	27.5
450	34	34.3
400	41.5	41.5
350	49	48.5
300	56.5	56

If Owen and Liu's results are correctly represented by Fig. 2, and I believe they are, then there is a difference of 3.7% between the two curves at 550° C. If two X-ray researches can differ by this amount at 550° C., and can be said to agree sufficiently well to be represented by a single curve, is it fair to criticize the metallographic work as inconsistent, as the authors do on p. 153, because a second investigation displaced the previously determined solubility of germanium in copper at 300° C. by 0.5%?

In my opinion, the authors have placed too much stress on comparing recent X-ray work with less recent micrographic work. They have neglected recent micrographic work which agrees with X-ray work, and they have not admitted discrepancies between different X-ray researches on the same system. The resulting picture is misleading. I see no reason to change my opinion that the two methods should be used in conjunction.

To turn to more general points, the authors are satisfied that our fears concerning the purity of filings are unfounded. It so happens, however, that the authors' experience has been mainly with relatively well-behaved metals,

* E. A. Owen and Y. H. Liu, *J. Iron Steel Inst.*, 1949, 163, 132.

† E. A. Owen and A. H. Sully, *Phil. Mag.*, 1938, [vii], 27, 614.

for which contamination problems are not serious. The fact that contamination effects have been absent in the Bangor experiments does not mean that no such effects can be encountered elsewhere with other materials. The extent to which contamination may affect X-ray results depends entirely on the alloy system concerned; a speck of soot from an industrial atmosphere falling on to copper-zinc filings will have no effect, beyond making the total of the constituents determined by analysis low. With certain iron alloys, some of the filings might be converted into an austenitic steel. With the authors' experiments confined to copper, silver, gold, pure iron, and lead, little effect is to be expected at low temperatures even if oxygen, carbon, and nitrogen are present. For aluminium, the authors refer to experiments which indicate that differences of as much as 0.0004 Å. exist between the lattice spacings of coarse and fine particles. These filings were presumably annealed in glass, and no analyses for the different grades of filings are given. Experience at Oxford has shown that the lattice spacings of aluminium powder are erratic after annealing at 500° C. in glass or silica, owing to absorption of silicon, which lowers the lattice spacing. Results are erratic because they depend on how much of the powder is in contact with the glass, on the time of annealing, and on the closeness of packing. The effect is prevented by using a lining of alumina inside the glass tube.

Professor Owen and Mr. Morris are precipitate in inferring that where pure metals show no contamination, the alloys behave similarly. Magnesium-cadmium alloys with about 33 at.-% cadmium are attacked by air with the formation of a complex nitride much more rapidly than either of the pure metals. The nitride phase penetrates the crystals along crystallographic planes, and clearly must alter the composition of the alloy matrix. Other similar cases are known. Their statement that X-ray examination can test for soluble impurities as accurately as any method of analysis of small quantities is misleading. It is only where lattice distortion is appreciable that the X-ray test is sensitive. This also applies to tests for segregation. For the solid solution of silver in aluminium, for instance, the lattice spacings up to about 10 at.-% are constant. How would the authors' generalization apply to this system? Again, it is an advantage that the microscopical method uses specimens of a size sufficient for a complete chemical analysis where necessary (except for very rare metals). In view of the fact that frequent reference is made in the literature to the analysis of the actual specimens used for microscopical examination, I find it hard to understand the authors' assertion that no tests for contamination are available in the microscopical method.

Problems due to volatilization from filings are often more serious than suggested by Professor Owen and Mr. Morris. It is true that, if an equilibrium vapour pressure is set up, actual loss is minimized by minimizing the dead space in the annealing tubes; this is obvious. It is, however, only true provided that the volatile component does not react with the material of the tube. For instance, magnesium vapour reacts with silica or glass to form Mg_2Si , and is removed from the system. More magnesium therefore distils, and over a lengthy annealing period the continuous distillation may be appreciable, leading to composition changes in the alloy. The authors, in arguing as though their own results on relatively stable alloys can be generalized to apply to all systems, have not convinced me that the sources of uncertainty regarding purity and composition of filings which were discussed at the Royal Institution in 1942 do not exist. They do exist, and are not only possible, but are often encountered. Tests for such errors should be made on each system investigated, and not omitted because the errors do not show up with, for example, gold alloys.

One further comment is necessary, concerning the use of polished surfaces

in the metallographic method. The authors' remarks are part of an old story, well-known to generations of physical metallurgists, whose accumulated experience cannot be neglected. Apart from certain steels, where it is known that transformations may be induced in the surface layers by overheating during metallographic transformation, I myself have never encountered an example of a microstructure giving rise to erroneous interpretations of the equilibrium state simply because of the presence of a somewhat deformed surface layer, some if not all of which is removed by etching. It is necessary to be quite clear about the use of unetched specimens. It often happens that, in a polished, unetched specimen, no metallographic features can be distinguished. The surface is just a mirror, and etching is needed to reveal the constituents. In such cases unetched specimens are never used in an attempt to infer the constitution. It also may happen that small particles of a second phase may be seen in the unetched condition, but that etching, because of its general attack on the matrix, or because it dissolves out the particles, makes them more difficult to see. In such cases the metallographer is rarely satisfied until he has produced a satisfactory etching reagent, but, having satisfied himself that the results from etched and unetched specimens agree, he may find it convenient to use unetched specimens for routine examination. The use of unetched specimens is simply a convenience, resorted to only after tests have proved that they give the same answer as etched samples; in other work, it may form part of a preliminary routine examination as Dr. Hume-Rothery has said.

Finally, the question of strain-induced precipitation during preparation giving rise to abnormally low solubility values may be examined. This source of error is improbable, for the following reasons:

(i) The general tendency is the other way about. In specimens annealed at low temperatures the microscope tends to miss fine precipitated particles. Since it is difficult to see particles precipitated at 300° C., anything precipitated at room temperature from a homogeneous alloy would be invisible, and the alloy correctly classed as homogeneous.

(ii) Where diffusion rates are sufficiently high for precipitation to occur at room temperature, e.g. in some age-hardening alloys, particles present after prolonged annealing, even at low temperatures, will be relatively large, and easily differentiated under the microscope from any effects due to incipient precipitation over a short period at room temperature, or the temperature reached in careful preparation.

The points discussed in this paper indicate that the quality of the X-ray work carried out at Bangor is very high, and that adequate tests are made and adequate precautions taken. They do not prove that, in general, the X-ray method is more reliable than the metallographic method. In my view, any such attempted generalization is useless, as the merits of either method depend on the problem under investigation. Both should be used together, and the choice of which is to be the main method of attack will be decided by the peculiarities of the particular system involved.

DR. K. W. ANDREWS,* B.Sc., A.I.M. (Member): The paper reveals the high standard of experimental work which Professor Owen and his collaborators have continuously maintained over a long period. Any criticisms I may make are, therefore, only directed at some of the authors' conclusions, in particular the suggestion that the X-ray powder method alone is more likely to lead to a diagram representing the true state of a system than the classical metal-lurgical methods. It still seems to be truer to experience to suggest that a

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discriminating use of *both* methods of experimental approach is more desirable than the use of either alone, and that as far as possible different methods should be used in conjunction. In some instances it is clear that an equilibrium diagram has been accurately determined by the X-ray powder method alone, whilst other systems have been more successfully studied by other methods, or by the application of more than one experimental technique. Much depends on the individual features of a diagram under investigation, and there can be no certainty beforehand as to which experimental method is going to give the most reliable results. Hence the necessity of using different methods so that if agreement is obtained there is additional confirmation, and if agreement is not obtained a satisfactory explanation can be sought, e.g. in terms of phases which decompose on quenching.

The authors refer to the systems copper-zinc and silver-zinc (p. 154), and suggest that these systems are unsuitable for investigation by *any* method involving the use of quenched specimens. They imply that it is not the X-ray method itself that is at fault, and this is undoubtedly true if the photographs are taken in a high-temperature camera. They claim, however, that the method using quenched filings not only supplies information about the identity of constituents, but also indicates whether the alloys have reached thermodynamic equilibrium (p. 153). This statement needs qualification, since, in the case of the two systems referred to, the powder photographs presumably gave no indication that they did not represent equilibrium at the quenching temperature, and thus, in fact, deceived the investigator who did not realize that they represented an approach to thermodynamic equilibrium corresponding to a much lower temperature! Nor are the authors correct in suggesting that the specimens examined by the classical metallurgical methods will necessarily lead to ambiguous conclusions as surely as the quenched filings examined by the powder method. The appearance of the microstructure of a phase which has decomposed on quenching is quite distinctive and very different from the appearance of samples where two phases have been in equilibrium at the temperature from which the specimen has been quenched, and no decomposition has occurred. This point will be made clearer by reference to a photograph of a silver-aluminium alloy in a paper by Hume-Rothery and others.* Here, the original grains of ζ are quite readily distinguishable from the background which may contain ζ as a decomposition product of β . Some of the silver-zinc decomposition structures were similar. Indeed, the presence of the decomposition structure provides useful information about the diagram itself; the fact that a phase has decomposed on quenching is an indication of what to expect at lower temperatures. Quite naturally, any confirmation that can be obtained by means of a high-temperature X-ray camera will also be acceptable, and no one will deny that this should be done whenever possible. The authors' contention about the systems copper-zinc and silver-zinc is not, however, supported, since both of these systems were, in fact, accurately determined by the classical methods (in spite of decomposition on quenching), whereas they were not accurately established by the X-ray methods!

In the paper by Dr. Hume-Rothery and myself† on the silver-gallium alloys, the solid-solubility curve from which has now been incorporated in Professor Owen's Fig. A (p. 678), we appear at first sight to have made an incorrect statement. We say: "The present work shows that the solubility of gallium in silver diminishes more rapidly than had been indicated by *any* of the earlier investigations" (p. 140). The phase boundary is to the gallium-

* W. Hume-Rothery, G. V. Raynor, P. W. Reynolds, and H. K. Packer, *J. Inst. Metals*, 1940, **66**, Fig. 11, Plate XL (facing p. 224).

† W. Hume-Rothery and K. W. Andrews, *J. Inst. Metals*, 1942, **68**, 133.

rich side of that of Owen and Rowlands for the temperature range 615°–300° C., which was the lowest temperature at which these authors determined the boundary. Our statement at that time was, however, correct, because the rate at which the solubility decreased with decreasing temperature was certainly greater than that suggested by the work of Owen and Rowlands in their original paper. In any case, we had ourselves determined the boundary down to 211° C. Owen and Morris have now adjusted their boundary and extended it down to 211° C.—actually making use of our own determination of the lattice parameter of a two-phase alloy at 211° C. Their phase boundary over the temperature range in question is now shown to the silver-rich side of ours. The differences increase from about 0.5% at the peritectic temperature to approx. 0.7% at the transformation temperature, and just over 1% at 200° C. These differences are not excessively large, and might be within the limits of experimental error, although one might have hoped for slightly closer agreement.

The limitations of the method using lattice-parameter/composition curves should be fully appreciated, and many of these limitations have been stressed elsewhere. In particular, there are the changes that may occur owing to Brillouin-zone effects, or to the appearance of ordered structures—regions of composition near to certain simple atomic ratios are suspect. Inaccurate results might also arise where there is at first an increase in solubility with decreasing temperature and then a decrease in solubility. If the temperature at which the change in direction occurs is somewhat low, the boundaries in this region may be inaccurately determined, as the alloys which should be homogeneous will be difficult to get into true equilibrium, where they have been duplex at higher temperatures. The same difficulties might apply to any method of investigation in this region; but long-period annealing treatments of lump specimens, or of powders, would seem to be indicated. Another possibility is the preparation of samples from powders of the pure metals mixed in the appropriate proportions and sintered at the temperature in question. Otherwise this is a hypothetical case where both X-ray methods and the classical metallurgical methods may give incorrect results.

The limitations of the metallographic methods, to which the authors call attention, are also generally well known to investigators who employ them in equilibrium-diagram determination or in other work. It may be of interest to observe that in the examination of certain austenitic steels microscopically we have found no evidence of the change of face-centred cubic γ to body-centred α which could have occurred on preparation of the surface, but the evidence is readily available from X-ray examination of the surface. Evidently the α is distributed on a sub-microscopic scale. On the other hand, any α originally present is readily distinguishable. The microscope still gives a substantially correct representation of the condition of the alloy at the quenching temperature. The size and distribution of particles is an indication of the manner in which they have formed and whether they represent a true equilibrium condition.

From the point of view of an industrial laboratory not primarily concerned with the determination of equilibrium diagrams, the questions raised are still of great interest. For instance, frequent use may be made of diagrams which need to have been reasonably accurately determined. There are many related problems in which the application of X-ray and microscopic methods in conjunction has led to the successful identification of constituents. From this standpoint, not only the actual presence of a constituent, but the form of its distribution throughout the matrix and its mode of formation are important, as many industrial uses obviously depend on properties affected by these aspects of the structure.

DR. J. W. CHRISTIAN,* M.A. (Junior Member): I should like to consider a little more fully the relative sensitivities of the two methods of determining equilibrium diagrams. Professor Owen and Mr. Morris have pointed out correctly in their paper that the accuracy of the X-ray method is determined (i) by the precision with which an individual lattice spacing can be determined, and (ii) by the slope of the lattice-spacing/composition curve. The accuracy of an individual determination is usually about 1 in 30,000, so that we may say that the uncertainty (Δc) with which the boundary may be located by the spacing method is given by:

$$\Delta c = \frac{a}{30,000 \left(\frac{da}{dc} \right)}$$

The final accuracy of the boundary is limited by the accuracy of the chemical analysis of the alloys used to determine the spacing curve. It is difficult to assess the error resulting from this; analysis figures are usually given to two places of decimals, but except in the most favourable conditions it is unlikely that the figure is significant to more than 0.1 wt.-%. This may represent more or less than 0.1 at.-% of a constituent, but for the sake of comparison I have assumed the latter figure as the limiting accuracy in ordinary circumstances of an individual boundary determination. The use of a method with a sensitivity appreciably greater than this will not lead to any greater accuracy in the placing of the boundary, though in a very few cases with a nearly vertical boundary the greater sensitivity may enable one to decide on the direction of slope.

I have calculated Δc defined as above for the solubility limits of various elements in aluminium (data taken from Axon and Hume-Rothery †), and in copper, silver, and gold (data taken from the various papers of Professor Owen and his collaborators).

Of 8 aluminium solid solutions considered, 4 had $\Delta c < 0.1\%$, 3 had $\Delta c > 0.1\%$, and there was one borderline case with $\Delta c \sim 0.1\%$. For 13 solid solutions in copper, silver, and gold there were 8 cases with $\Delta c < 0.1\%$, 3 with $\Delta c > 0.1\%$, and 2 cases with $\Delta c \sim 0.1\%$.

It follows that the sensitivity of the X-ray method is insufficiently great to give an error less than the analytical error in more cases than is commonly supposed. Professor Raynor has already mentioned the case of silver dissolved in aluminium, where, to the order of accuracy of measurement, there is no change in the lattice spacing as the solid-solution region is traversed.

We have to compare the above figures with those for the microscopic method. Professor Owen found in iron-nickel alloys—a not very favourable case—that he could detect 0.5% of a phase by X-rays. The microscopic method is usually considered to be a more sensitive disappearing-phase method than X-ray diffraction, and it is therefore safe to assume that 0.5% of a phase can nearly always be seen under the microscope. The sensitivity of this observation in terms of the atomic composition of the solute element depends on the width of the two-phase region in at.-%. If the two-phase region is less than 20 at.-% in width, then 0.5% of a phase will represent a difference of < 0.1 at.-% of a component, and the accuracy of the boundary is limited only by the analytical error. There are many equilibrium diagrams where the two-phase fields are less than 20 at.-% in extent and where therefore the microscopic method does not suffer in comparison with the X-ray method as regards sensitivity. It should be noted in fairness, however, that the attainment of the ultimate accuracy is more difficult in a disappearing-

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† H. J. Axon and W. Hume-Rothery, *Proc. Roy. Soc.*, 1948, [A], 193, 1.

phase method, which requires the preparation and heat-treatment of a large number of alloys of slightly different compositions near the phase boundary concerned. The differences in phase-boundary determinations by different authors using the same or different methods are usually considerably greater than the 0.1 at.-% used above.

To turn to another point I should like to emphasize the greater difficulties which are encountered in equilibrium-diagram work with reactive alloys, particularly high-melting transition-metal alloys. In my opinion Professor Owen's conclusions, which are based largely on work with relatively stable copper, silver, and gold alloys, certainly do not apply to these cases. In annealing specimens at high temperatures it is extremely difficult to prevent contamination by oxygen, nitrogen, or other gases, particularly when it is no longer possible to use sealed-off silica capsules. The danger of contamination by gases is much increased if the specimen is in the form of a fine powder, and quite small amounts of gaseous impurities may have a marked effect on the lattice spacings. These impurities are not easily detected by analysis. An additional effect is oxidation, which often occurs on quenching, and though not serious in a lump specimen, from which the surface layer can easily be removed, may necessitate an inconvenient and less rapid quenching procedure in the case of a powder.

Finally, I should like to point out that in some cases neither method seems at present to be capable of giving us true phase boundaries. This is particularly true of cobalt-rich alloys. The investigations of Edwards and Lipson* have shown that the phase change from close-packed hexagonal to face-centred cubic cobalt does not appear to take place at constant temperature as required by the Phase Rule. Pseudo-phase boundaries, usually determined by thermal-arrest methods, are plotted in a large number of systems, but it is doubtful if any of these represent equilibrium-diagram boundaries. Alloys quenched from the homogeneous face-centred cubic region above the close-packed hexagonal region usually show both face-centred cubic and hexagonal lines, though the properties of the phases and the parameters vary with the conditions. The same alloys examined microscopically appear generally to be one-phase. This transition is not yet fully understood, but serves as an illustration of the limitations of both methods.

MR. H. J. GOLDSCHMIDT,† M.Sc. (Member): The major issue is the relative value of using powders or solid blocks for determining equilibria. Professor Owen's conclusion that the powder method, even when used on its own, is the most suited for equilibrium-diagram investigations is very comforting, not least because it falls completely into line with Dr. Bradley's work, and at present we still follow it to some extent. I can fully confirm that the rate of obtaining equilibrium in the powder is generally more rapid than in the block, and I could quote many examples to support the authors' thesis; particularly striking is the case of steels, where, for instance, austenite can be retained in the lump, while for filings the same heat-treatment would have decomposed it. The broad explanation appears to be that in the mass the constraints exercised between neighbouring grains produce a tendency to resist the atomic-volume changes involved by the transformation. In permanent-magnet alloys, for example, of the Alcomax type, the added magnetostrictive force makes interference between crystallites particularly intimate; and our X-ray tests have shown that it is almost impossible to obtain true equilibrium in the mass within a reasonable time, while it is much easier to do so in powder form. For true equilibrium investigations and rapid surveys, the powder

* O. S. Edwards and H. Lipson, *J. Inst. Metals*, 1943, 69, 177.

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method is certainly supreme, but the difficulty arises where correlation with practical properties such as hardness, tensile strength, &c., is required. I suggest that the best solution is always to investigate both types of sample simultaneously—the powder as the pilot sample and the lump as the practical companion during heat-treatment—while realizing fully that the lump may only have partially approached the equilibrium shown by the powder. We always use this method now in our phase-diagram work.

A further technique is what might be called the "powder-in-block" method, which we use on steel samples. Two or three fine holes are drilled at different diameters of the sample bar and packed with filings of the same material; the block is then heat-treated as desired and the powder is then removed from it and X-rayed, while the lump is examined metallographically in the areas adjoining the holes. In fact, the holes containing the powder can be used to accommodate a thermocouple for parallel thermal tests on the specimen. With such powders removed from quenched lumps it has been possible to explore the interior of a sample, and, for example, to plot "contour lines of equal austenite content" as a function of depth below surface. A further method, not mentioned by Owen and Morris, is the use of small rods or wires instead of filings. These are examined directly by the X-ray powder method and as metallographic specimens.

There seems to be one slight contradiction in the authors' argument. They criticize Hume-Rothery and Raynor (on p. 154) for stating that certain alloys "are unsuitable for X-ray examination of quenched filings", because in that case they would also be unsuitable for examination by any other method, whether on powders or lump. I think this is not so, as a high-temperature phase, which decomposes on quenching a powder, has a better chance of being retained in the lump; the greater sluggishness of reaction gives the lump an advantage in quenching experiments for the very same reasons that favour the powder in determining low-temperature equilibria.

I agree that the method of surface preparation of block specimens presents a fundamental difficulty, and that almost any type of polish or cold work is liable to give misleading results. In ferrous metallurgy this difficulty is very pronounced. The authors mention (on p. 164) the fact of intense surface heating through so-called "cold work". I can confirm this from experience with certain steels, which for low-temperature equilibrium consist of ferrite plus carbide, while surface grinding produces a thin top layer of austenite, quite undetectable under the microscope but clearly visible by X-rays.

I would not perhaps reject etching techniques to remove the cold-worked layer for X-ray test on the block as completely as the authors seem to do, since deep etching is often valuable. Also, electrolytic etching in selected reagents has great possibilities for preparing X-ray block samples.

In the "Conclusions" work is mentioned proving that in the solid block approach to equilibrium differs from one crystal to the next. Do the authors refer here to the micro-beam technique? Orowan's and Guinier's polygonization work has also provided valuable evidence of crystal-to-crystal variation, and we have ourselves obtained further proof for such variations through what is believed to be a new type of X-ray evidence.

Is it too daring to suggest that in the polycrystalline mass perfect equilibrium can theoretically never be achieved, owing to the mere presence of crystal boundaries and the discontinuity in lattice orientation and boundary-zone stresses they imply? It seems that ideal equilibrium can only exist either in a single crystal or in a fine powder in which the crystals are physically separated.

Regarding the powder technique, Owen and Morris discuss only the preparation and heat-treatment of filings. But with many metals, such as hard or brittle high-melting ones, filing is impossible, and either crushing or drilling

is necessary; failing that, nothing remains but the block examination, which re-emphasizes its necessity in spite of its weaknesses. What material should be used for the small vacuum container in which the powder is heat-treated? Silica tubes are generally accepted, but is there not sometimes a danger of contamination, e.g. with aluminium-bearing alloys? Moreover, silica becomes useless much above 1000° C., and I should appreciate Professor Owen's advice on the high-temperature heat-treatment of powders. We use a continuously evacuated furnace for the powders, but small evacuated alumina tubes, instead of silica, are a possibility.

The methods described in Section III of the paper, of testing for contamination from lattice-spacing constancy prove, I think very well, the case for the spacing method of phase-boundary determination. But does this method not mainly refer to the case of a *substitutional* solid solution? With small atoms such as carbon in interstitial solution the uncertainty enters of erratic results through defect lattice-formation, which in practice can cause spacing fluctuations even in the two-phase field that are very difficult to eliminate. Moreover, the spacing method of boundary location relies on a considerable difference in atomic size between the two elements and can become rather insensitive in the case of similar atomic sizes, e.g. two co-existing body-centred cubes of similar dimensions, though of quite different compositions, can badly affect the accuracy.

In this connection may I raise the question of the best technique of precision lattice-spacing measurement? Can film viewing by eye through the travelling microscope be beaten in accuracy by a photometer noting the peak positions of lines?

The "disappearing-phase" method, as the authors say, is generally less sensitive for boundary location than the lattice-spacing method, but I think there are cases when it is more so. As it depends on the lower visibility limit of the strongest line of the second phase, the Geiger-counter technique may yet give new life to this method and increase its accuracy.

I should like briefly to mention a simple technique I found useful in powder photography, to increase the visibility of a weak second phase, and thus, among other things, to render boundary location more precise. That is to stop the specimen-rotation, at least for part of the time of exposure. It is thus possible to render a weak phase visible, which otherwise would have escaped detection, as it registers itself on the film in the form of one or two strong spot reflections instead of almost invisible uniform lines.

I heartily agree with all the authors say about the value of the high-temperature camera in phase-diagram work, and am glad to see the very fine examples of diagrams determined with it (iron-nickel and aluminium-zinc). Does this not raise the question whether in principle the high-temperature camera should not always be used to check the results of quenching; failing this, in which cases and by what criterion is it ever safe to rely on quenching results alone? A complicating factor, with which we are also faced in our camera work, arises in deciding the minimum time for which the specimen ought to be held at the high temperature before equilibrium can be assumed and the photograph taken. The quench sample can be held at temperature for weeks if desired before quenching, but this is not so easy in a camera much in demand.

The authors reject Hume-Rothery and Raynor's criticisms in several places on the grounds that they are examples of "misuse" of the X-ray method rather than difficulties inherent in it. On re-reading their papers, however, I am of opinion that Hume-Rothery and Raynor only meant to warn X-ray workers against such misuse and to urge them to take the necessary precautions, and in this sense they performed, I think, as valuable a service as the present admirable paper.

MR. H. P. ROOKSBY,* B.Sc. : I have spent a good number of years with X-ray technique and have considerable enthusiasm for the method, although I have no experience in its use for the determination of phase boundaries. The present paper is the work of enthusiasts for a particular physical method, and although in several directions the authors may have overstated their case and taken observations made by others out of their original context, I have no doubt this was done purposely in order to develop the argument that the X-ray method is a powerful one, if used with the necessary precautions, and with a recognition of its limitations. I think the authors would readily admit that any one method used alone for phase-boundary determination must really be less satisfactory than a combination of techniques. But their claim is that X-ray analysis itself is on the whole less liable to give misleading answers than other methods. I believe this is probably true in a majority of cases, provided that the technique itself is used with the care and devotion that Professor Owen and his colleagues have always employed.

As I see it, the authors' chief arguments depend upon the use of filings rather than lump specimens for X-ray examination and upon the adoption of lattice-parameter measurements rather than the disappearing-phase method for placing the phase boundary. Probably if X-ray technique is granted to be right there is little dispute that the lattice-spacing method is the preferable one. Here I agree with the point the authors make that it is no true criticism of X-ray technique to point to its misuse. Lengthy extrapolations should be anathema to any self-respecting physicist, and it should be an axiom of the method that no assumptions about the shape of the lattice-spacing curve are made. It should be determined in detail by experiment as close to the phase boundary as possible.

Turning to the filings question, I feel that the observations recorded were worth making, even apart from the objective of meeting criticisms that had been levelled at the use of filings. The controlling factor seems to me to be that the original ingot from which the filings are prepared has to be above reproach. If this is so, nearly everything else follows—and I must say I would be quite content with the ingots that Professor Owen makes. I think the authors make their point too that the achievement of equilibrium may well be more rapid in filings than in solid specimens, but in any event the proper time of heating is determined by definite tests.

On the question of retaining a high-temperature condition by quenching the authors also make a relevant comment. I have often met the argument that because the high-temperature phase is sometimes not retained the X-ray method is an unsuitable one. But so is the microscopic or any other method which depends upon quenching. At least the X-ray technique can be altered when the need arises by utilizing one of the high-temperature instruments now becoming available. From all points of view more X-ray measurements should be made at elevated temperatures, and there are good instruments being developed now which can do the job satisfactorily.

Finally, I sympathize with the authors' remarks about the preparation of sections for micrographic examination. In my opinion there is some truth in the observation that metallurgists occasionally forget the changes that may be wrought by the processes of surface preparation. Phase transitions can be caused by cold work, and it is often difficult to assess how deeply the metal has been affected. Unless this depth is known with certainty—and it would seem to me that this is commonly in doubt—the amount of etching to be done is uncertain too. We are examining an alloy at the moment which is face-centred cubic at high temperatures, and this condition is retained by

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quenching. At the slightest provocation transformation to the hexagonal close-packed structure takes place, and even deeply etched prepared surfaces show this form on X-ray examination. With surfaces quenched from high temperatures, however, X-rays disclose the cubic structure alone.

MR. J. CANTRELL* (Member): We are much interested in the difficulties experienced by some X-ray workers arising out of contamination from the file material, in reducing the test alloys to powder. We have suffered from a similar effect in powder-metallurgy work on a laboratory scale. Our troubles were completely eliminated, however, by the use of a metal-bonded diamond hand hone. These hones can be made with the diamond points very "proud", and the material being powdered never touches the bonding metal, thus avoiding the possibility of contamination. In extreme cases, where even a few tiny fragments of broken diamond cannot be permitted in the powdered specimen, the impurity may easily be removed by flotation in liquid of suitably high specific gravity. The use of diamonds, with their low coefficient of friction, ensures cooler cutting and avoids the sintering together of the metallic particles.

PROFESSOR W. R. D. JONES,† D.Sc. (Member): Many methods have been used in the experimental study of equilibrium diagrams, and the most common are the older method used by the metallurgist and the relatively newer method developed by the physicist.

This interesting paper is valuable, even if it does nothing more than draw attention to the differences between the two methods and the opposition which seems to exist between workers specializing in them. It should be pointed out that any method is legitimate if it provides correct information on which to establish the phase boundaries of an equilibrium diagram. Every method requires the development of a technique of high standard, a realization of its limitations, and a considerable experience to enable the experimentalist to appreciate the evidence. Unfortunately, the X-ray workers in many cases have neglected the older microscopical methods, and have been inclined to consider that a phase boundary could be established by using a very much smaller number of alloys than that considered desirable by those using the older method. The microscopist is apt to look with a certain amount of suspicion on the "filings" method, whilst the X-ray worker points out the obvious disadvantages of using the material in a massive form, particularly its liability to contain impurities which may not be distributed uniformly and the time taken to reach equilibrium. The obvious procedure is to use both methods in conjunction, if not by the same worker, then certainly by people of the same laboratories, expert in the respective techniques.

The summary which the authors give (on p. 153) of the position seems to indicate their belief that the X-ray method is more accurate than the microscopical method which they state to be qualitative rather than quantitative. However, it is generally on visual observations under the microscope that is based a suitable heat-treatment to affect the mechanical and physical properties of the material. Many of the criticisms which the authors make against the older methods in the preparation and etching of specimens are well appreciated and as far as possible precautions are taken to avoid them. The development of X-ray methods has had the indirect effect of causing an improvement in the technique of the older method. It is probably best to consider the two methods as being complementary, using one to make up for the deficiencies of the other.

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An interesting example of this combination is offered by some work carried out at Cardiff about twenty years ago on the copper-magnesium system, where a detailed examination by the older method (thermal and microscopic) was published * soon after an examination using X-ray methods by Grime and Morris-Jones,† and by Runqvist, Arnfelt, and Westgren.‡ The X-ray methods disclosed a solid-solution range extending on each side of the composition Cu_2Mg . The microscopical method failed to show any evidence of the existence of a range of solubility at this point. A fresh examination by the X-ray powder method was undertaken by Sederman§ at my suggestion, using the same alloys and in many cases the actual specimens which had failed to provide confirmatory evidence of the findings of the previous work using X-ray methods. Sederman's results were consistent with the existence of a homogeneity range though of much smaller extent than was suggested by Grime and Morris-Jones. It is possible that a re-examination of these alloys with improved technique and the use of the electrolytic methods of polishing and etching now possible may show some solid solubility.

THE AUTHORS (*in reply*): In his opening remarks, Dr. Hume-Rothery refers to the discussion on the use of X-ray methods in the determination of phase boundaries in alloy systems which took place at the Royal Institution in 1942, at which, he states, the general opinion of the meeting was that the microscopical and X-ray methods should be used in conjunction. We are certainly not opposed to this view, but, as he himself correctly points out, our conclusion is "that in determining an equilibrium diagram the *main emphasis* should be on the X-ray work, with microscopical examination used only as a secondary technique". This should not be taken as indicating that we advocate the use of the X-ray method alone. As stated on pp. 146 and 167, our purpose in writing the paper was to modify the emphasis placed on certain aspects of the work, the necessity for this being impressed upon us as a result of our recent researches on lump specimens, carried out after the Royal Institution meeting, to which reference is explicitly made in the paper. Moreover, both at that meeting and in Hume-Rothery and Raynor's original paper,|| the limitations of the microscopic method were hardly mentioned at all. Although it now emerges from the present discussion that these are in fact well known to metallurgists, it seemed to us that some mention of them at least was desirable and that a reassessment of the value of the two methods in phase-boundary determination was required.

Dr. Hume-Rothery states that we have supported our attack on the microscopic method "by statements and diagrams some of which appear misleading as to the relative merits of the two techniques". In the course of our reply we shall endeavour to show that there is no real ground for making this statement.

He also states that we have reached our conclusions mainly by presenting seven equilibrium diagrams chosen from those which we have examined, and suggests that this is too small a number of diagrams to enable satisfactory conclusions to be drawn. We would like to assure him, however, that the number seven was governed by considerations of space only and not by any desire on our part to restrict the comparison to cases which appear especially favourable to X-ray methods. The diagrams were actually chosen to meet

* W. R. D. Jones, *J. Inst. Metals*, 1931, **46**, 395.

† G. Grime and W. Morris-Jones, *Phil. Mag.*, 1929, [vii], **7**, 1113.

‡ A. Runqvist, H. Arnfelt, and A. Westgren, *Z. anorg. Chem.*, 1928, **175**, 43.

§ V. G. Sederman, *Phil. Mag.*, 1934, [vii], **18**, 343.

|| W. Hume-Rothery and G. V. Raynor, *J. Sci. Instruments*, 1941, **18**, 74.

the specific objections of Hume-Rothery and Raynor,* to illustrate the usefulness of high-temperature X-ray technique, and to show how difficult cases involving volatile constituents can be successfully tackled by the X-ray method. Later on in his contribution, Dr. Hume-Rothery has considered the whole of the work on the alloys of copper and silver which have been studied by X-ray methods at Bangor, and of which he has had personal experience, and with the exception of X-ray work in the β region of the systems copper-zinc and silver-zinc, concludes that in general there is very good agreement between the results obtained by the two techniques. Before going on to comment on this, however, it will be convenient to consider first the criticism and objections which he has offered on the diagrams published in our paper.

Silver-Gallium.—Dr. Hume-Rothery refers to the first investigation of this system published in 1934 by himself, Mabbott, and Channel-Evans, and emphasizes that nothing would have been gained by using the X-ray method at this stage because the quantity of gallium available was too small to permit the precautions which we say are necessary if the method is to be reliable. Apparently, however, he has not realized that practically all the work at Bangor has been carried out on extremely small quantities of material (there are many statements in earlier papers from this laboratory to the effect that the ingots prepared were of the order of 1 g. in weight), so that, as regards the determination of the solid-solubility curves, the conditions prevailing at Oxford in 1934 would seem to have been peculiarly suitable for the employment of the X-ray method. In fact, this characteristic of being able to deal successfully with very small quantities can be regarded as a further advantage of the method, particularly in the case of rare and precious metals.

Dr. Hume-Rothery, and also Dr. Andrews, point out that in our Fig. 7 we have omitted to include the solid-solubility curve obtained by them in 1942. The policy adopted in our paper was to compare the X-ray results with the data obtained by classical metallurgical methods, available at that particular time. Admittedly, this could perhaps be claimed to favour the X-ray workers, in so far as they were in possession of some knowledge of the form of a diagram at the time their investigations were begun, but in many cases this information was either incomplete or incorrect, and this was certainly the case with the silver-gallium system, since the boundaries proposed in 1934 were corrected in 1942 by the metallurgists themselves.

In Fig. A (p. 678) the solid solubility curve of Hume-Rothery and Andrews has been included. The history of this diagram is that (1) in 1934 Hume-Rothery, Mabbott, and Channel-Evans, by microscopical methods, propose the curve *ab*; (2) in 1940 Owen and Rowlands,† by X-ray methods, propose *cd*; (3) in 1942 Hume-Rothery and Andrews, by microscopical methods, propose *ef*; and (4) in 1949, Owen and Morris propose curve *gh*. The significant point is that the change suggested by (3) occurred after the first X-ray work had been published. Moreover, the change proposed by Owen and Morris in 1949 in the boundary determined by X-ray methods was prompted only by the suggestion of Hume-Rothery and Andrews that the original parameter/composition curve of Owen and Rowlands should be drawn with a slight curvature, and the fact that they (Hume-Rothery and Andrews) obtained the lattice parameter of a two-phase alloy quenched from 211° C. (the work of Owen and Rowlands did not extend below 300° C.). Contrary to Hume-Rothery's assertion, therefore, the curve of Owen and Morris owes nothing to the *microscopical* work of Hume-Rothery and Andrews, and the original lattice-parameter values of Owen and Rowlands are unchanged. He

* *Loc. cit.*

† Based on work done before 1937. (V. W. Rowlands, M.Sc. Thesis, University of Wales, 1937.)

is, however, correct when he states that "the lowest point shown on what they call the curve of Owen and Rowlands is really based on the lattice-spacing given by Hume-Rothery and Andrews". This is quite clearly stated in the text on p. 162: "The point shown at 211° C. in Fig. 7 has been deduced from our parameter-composition curve, using the lattice parameter in the duplex region at 211° C. determined by Hume-Rothery". Unfortunately, however, owing to an oversight in not correcting the parameter value given by Hume-Rothery and Andrews to 18° C., the solubility at this temperature was incorrectly deduced by us as 11.0 at.-% gallium; the corrected value of 11.8 at.-% is now given in Fig. A, and we are sorry for this error. As may be seen by comparison of this figure with Fig. 7, this changes the temperature of the $\zeta \rightleftharpoons (\alpha + \zeta')$ eutectoid transformation to about 375° C., in closer agreement with the value deduced by Hume-Rothery and Andrews by high-temperature X-ray work. It also produces better agreement over the lower-temperature range between our modified curve and that of Hume-Rothery and Andrews. The figure, therefore, shows the very close agreement of the X-ray work carried out by Owen and his collaborators at Bangor and by Hume-Rothery and Andrews at Oxford, but the quite pronounced differences in the two microscopic investigations conducted at Oxford.

With regard to Hume-Rothery's reply to the question asked in our introductory remarks concerning the rate at which the solubility of gallium in silver diminishes with decrease of temperature, we are aware that Owen and Rowlands' investigation did not extend below 300° C., whilst Hume-Rothery and Andrews's work extended to 211° C., but this is not the point at issue. No reference is made in the reply to the rate of diminution of solubility at the lower temperatures.

It is also pertinent to comment at this stage on Hume-Rothery's statement on the silver-arsenic system that the relative merits of the two techniques are not to be tested by comparison of X-ray work of 1949* with microscopical work of 1915. Apparently this last date must now in the silver-gallium system, be extended to 1934†—indeed, it appears to be implied that the only fair comparison is between practically the only X-ray work on a given system with microscopic work which after many years' investigation has eventually obtained substantial agreement with it, and that therefore the latter technique is equally satisfactory. Furthermore, that any slight discrepancies which may then exist are to be attributed to faulty X-ray work. We feel ourselves that whilst X-ray work of 1940 may reasonably be regarded as "early work" in this field, the same is not true of microscopical work of 1934, and not even of 1915. Desch‡ says "Sorby was successful in devising a suitable technique for the preparation and examination of microsections, and his latest publications (1882, 1886, 1887) contain photomicrographs which have hardly been surpassed in excellence by later workers". In view of this, therefore, it is difficult to avoid the conclusion that there is something fundamentally unsatisfactory in the application of the microscopic method as a whole to phase-boundary determination to produce the divergence which is apparent between the work of 1934 and 1942. Lack of equilibrium in the lump specimens would seem to be ruled out as a cause of these discrepancies, since the method of testing for this described by Hume-Rothery is stated to be entirely satisfactory.

Silver-Aluminium.—As Dr. Hume-Rothery remarks, this diagram (Fig.

* Actually 1937. *Loc. cit.*

† As will be clear from the preceding remarks the "latest X-ray information of 1949" to which Dr. Hume-Rothery refers is, with the exception of one point at 211° C., work completed before 1937 (*loc. cit.*).

‡ C. H. Desch, "Metallography", p. 3. London: 1942 (Longmans, Green and Co., Ltd.).

B, p. 681) was discussed by himself and Raynor in 1941. It was included as Fig. 3 of our paper to show, as stated on p. 158, that it did not justify the conclusion arrived at by them that "as the temperature is raised the older methods become relatively more suitable, and the X-ray methods may well be confined to cases where the solubility range is very small or the boundaries nearly vertical". The position in this system, however, is not quite the same as it was in 1941, as claimed by Hume-Rothery, since the boundaries given by Foote and Jette have been confirmed over practically the whole temperature range by the independent work of Owen and Roberts.

Dr. Hume-Rothery has suggested that we have omitted from our diagram the higher-temperature work of Hume-Rothery, Raynor, Reynolds, and Packer, where it is claimed to be accurate, and included the low-temperature work where it was in error; but in fact we have given in our diagram the full curve of Hume-Rothery, Mabbott, and Channel-Evans, and as Dr. Hume-Rothery is aware, the later work coincides exactly with this above 450° C., and the two curves are superimposed. This is also clear from the text, where we state (p. 158) that the point *C* is found at 20.5 at.-% aluminium by both Hume-Rothery and Raynor and by Hume-Rothery, Mabbott, and Channel-Evans.

Silver-Arsenic.—The first point raised by Dr. Hume-Rothery has already been dealt with. Secondly, he comments on the reproducibility of the X-ray methods at the higher temperatures. The two diagrams silver-arsenic and copper-arsenic were included in our paper to show the close agreement of two independent X-ray investigations of two very difficult systems, viz. systems containing a volatile constituent. Judging from the fears expressed by Hume-Rothery and Raynor in 1941 regarding the composition of the powders, one would scarcely expect agreement at all with materials such as these, since it is hardly likely that the samples would have been contaminated or have changed their composition in the same way in different investigations.

Hume-Rothery remarks "the authors emphasize that they have not shirked the analysis of their filings". Actually, however, no statement to this effect was made by us in connection with the silver-arsenic system (pp. 158-160), although it is true that on p. 149, in dealing with another point, we say "... the actual filings of many samples were analysed". The original paper, referred to in Fig. 5, shows that no chemical analysis was carried out in the investigation of the silver-arsenic system.

The probable error of ± 0.15 at.-% quoted in connection with this system for the solid-solubility values was the average over the range of temperature investigated. We agree that this estimate is too small for the value at 595° C. The point at issue, however, is not the discrepancy of ± 0.5 at.-% between the two X-ray investigations (actually the experimental points given in Fig. 5 agree better than this even at the higher temperatures), but the much more serious differences amounting up to 3 at.-%, between the X-ray and the microscopical investigations.

Copper-Arsenic.—Dr. Hume-Rothery remarks that the work of Hanson and Marryat and of Hume-Rothery, Mabbott, and Channel-Evans on this system was in error almost certainly as a result of insufficient annealing. It would appear that the elaborate precautions described by Hume-Rothery to determine whether the specimens had reached true equilibrium had proved inadequate, or that the preparation of the specimens for microscopical examination had disturbed the structure. We thank Dr. Hume-Rothery for drawing our attention to the work of Mertz and Mathewson on this system. The agreement of this work with that of Owen and Rowlands and of Owen and Roberts, at the higher temperatures, is very satisfactory, and would not appear to bear out Dr. Hume-Rothery's conclusion that the X-ray method is not very precise in this range. The "marked divergence" of 0.4 at.-% at

300° C. to which he refers is actually somewhat less than the uncertainty in the microscopical method at this temperature, and the change in direction at 380° C. observed in the Bangor work would seem to be associated with a change in the structure of the β phase similar to that found by Mertz and Mathewson in the analogous copper-antimony system.

Copper-Indium.—This system is interesting because the X-ray work suggests a higher solubility of indium in copper than that given by microscopical work at the lower temperatures. We have carefully checked our Fig. 6, and cannot find any grounds for Hume-Rothery's statement that owing to an error in drawing we have slightly exaggerated the difference between the X-ray and microscopical investigations.

We would refer Dr. Hume-Rothery to our reply to Professor Raynor, below, for comments on the criticisms made of the aluminium-zinc and iron-nickel systems, but we must protest against the implication of his statement that the "authors have gone back 35 years to find faulty microscopical work in the system silver-arsenic".

Aluminium-Zinc.—We find it somewhat difficult to understand Professor Raynor's remark that we have hardly sufficiently acknowledged what the X-ray investigators owed, before starting work, to the previous classical researches, since we have expressly stated on p. 155 that it was known from work by ordinary metallurgical methods that β transforms on quenching and that Tanabe's diagram, which we reproduced, was the twenty-fifth contribution on the system by classical metallurgical methods.

Professor Raynor is also mistaken in stating that we have reproduced Tanabe's diagram as an illustration of an incorrect piece of work, and Owen and Pickup's diagram as the correct one. What we did was to reproduce the most reliable diagram of the aluminium-zinc system which was available at the time the X-ray investigation was begun, indicated the modifications suggested by the X-ray work, and simply stated that these were later corroborated by classical metallurgical methods. Professor Raynor is very anxious that we should not lose sight of the fact that the latter methods were capable of getting the right answer too. If this is so, we are tempted to remark that it took them an unconscionably long time to do so. In actual fact, however, we do not think that the classical methods are capable alone of getting the right answer here, or at least not the complete answer, since this involves knowing the structure of the phases, and it would seem to us that the later work by classical methods owes a great deal in this system to the X-ray work.

Professor Raynor then says we have not mentioned the work of Owen and Iball, and has quoted from their paper statements which were later found to be incorrect. We think, however, that in the interests of fairness, he might also have quoted other sentences from their paper to the effect that it was only a preliminary and incomplete survey of the system, and that the authors were well aware that the high-temperature technique was at that time imperfectly developed. This investigation was actually amongst the first ever to be done at Bangor on alloy systems at elevated temperatures, and we therefore think it is excusable not to have included the results of this work in our diagram.

Professor Raynor does not consider Fig. 1 as being entirely fair. We think, however, that it would have been fair to compare the first X-ray investigation of this system, which was considered reliable by the X-ray workers, with the first classical investigation which was considered reliable by the metallurgists. We have actually done a little better than this, as we have avoided comparison with Hanson and Gayler's diagram, since it appeared that difficulties might have arisen through the decomposition of the β phase,

and have instead used Tanabe's diagram, as the methods employed by him seemed to have overcome this difficulty.

It is true, as Professor Raynor remarks, that in Owen and Pickup's work the two limbs of the ($\beta + \gamma$) boundary did not quite join up, as indicated in our Fig. 1, and we must apologize for this error in the drawing which was not intentional. The true position was as indicated in the text (p. 155). It is significant, however, that it was X-ray work which first suggested the possibility of a completely closed loop, and it was only later that its existence, first proved by Fink and Willey by electrical-conductivity measurements, was established by microscopic methods. As stated in our paper, therefore, there is no doubt that the X-ray method was the means of clearing up a difficulty which had baffled the metallurgists, and to establish this point we cannot agree that our Fig. 1 gives a false impression.

Iron-Nickel.—Professor Raynor remarks that it is hardly correct for us to state that before the work of Owen and Sully numerous investigations had been made on the binary system iron-nickel. Actually, we did not say binary; indeed we would be very glad to be referred to *any* investigation on a pure binary system.

He then says that no micrographical examination appears to have been made on pure alloys and no direct comparison between the two techniques (viz. this and the X-ray method) can be made. He is, however, mistaken in inferring that any such comparison was made in our paper; there is no mention of pure microscopic work at all in the section on this system. All we have done is to compare the selected iron-nickel diagram of Marsh, which included the results of many investigations by thermal, dilatometric, microscopic, and magnetic methods (and one tentative X-ray investigation), with those of Owen and Sully, and of Owen and Liu by X-ray methods alone.

Professor Raynor then points out that we have failed to mention that X-ray investigators have produced quite different results for the lattice spacings and solubility limits in this system. Owing to restrictions of space, it was impossible for us to include detailed references to all the investigations which have been made on this system, but since the implication is that the X-ray method is as unreliable as the classical methods, we will consider this point in some detail.

It should be noted in the first place that although the iron-nickel system is in principle very simple, the difficulty of establishing equilibrium conditions makes it possibly one of the most difficult from the point of view of the exact location of the phase boundaries. Marsh* says: "There are no conclusive data which would permit location of the equilibrium boundaries with any useful degree of certainty". That was the position in 1938, so that it appears that at that time the classical methods, which had been used in by far the greater number of investigations on this system, were incapable of providing a solution to the problem. Secondly, the system is one in which decomposition occurs on quenching, so that according to Raynor's own statement† it is unsuitable for examination by X-ray methods employing quenched specimens alone. It would seem to us, therefore, to labour the point somewhat for Raynor to wish us to include all the earlier and different lattice spacings and solubility limits which have been produced by this admittedly incorrect method. Actually, it does not seem to have been appreciated that this and the aluminium-zinc diagram were given in our paper to show the usefulness of the X-ray method when high-temperature technique is combined with work on quenched specimens, and the correct method of arriving at the

* J. S. Marsh, "The Alloys of Iron and Nickel", Vol. I, p. 54. New York and London: 1938 (McGraw-Hill).

† W. Hume-Rothery and G. V. Raynor, *J. Sci. Instruments*, 1941, 18, 74.

value of the X-ray work is to consider the results obtained with *this* kind of investigation and not by quoting the earlier results obtained by methods which violate Raynor's own canon.

Professor Raynor also appears to criticize us for omitting to point out that the work of Owen and Liu was carried out by the vanishing-phase method. The two techniques available in the X-ray method and the conditions under which they are employed were, however, described in Section IV of the paper. The iron-nickel system happens to be one where the vanishing-phase method is more suitable, but in a comparison of the results of the X-ray method as a whole with those obtained by the classical methods, such as was made by us, it seems somewhat invidious to single out for special treatment the technique adopted in any one particular investigation. However, since this point has been raised, it is perhaps worth noting that the X-ray method has the advantage of being able to choose between two alternative techniques.

Professor Raynor has also pointed out discrepancies between the work of Owen and Sully and of Owen and Liu. He remarks that "This work [viz. that of Owen and Liu] showed that the $\alpha/(\alpha + \gamma)$ boundary at 300° C. given by Owen and Sully was in error by about 3%". The relevant passage from Owen and Liu's paper* is (p. 134): "A more detailed survey of the α boundary at temperatures below 400° C. would be desirable; the necessary alloys were not available for this investigation. Since the lines in the spectra indicated that the materials had not reached their final equilibrium states, the position of the α boundary in this region must not be regarded as having been finally settled. According to the two investigations so far conducted in this laboratory, it lies between 5.8 and 6.9 at.-% Ni at 350° C., and between 4.8 and 7.5 at.-% Ni at 300° C." Professor Raynor is therefore quite incorrect in making a dogmatic statement on this point; his conclusion appears to be based on too cursory a perusal of the paper concerned.

Furthermore, this mistaken conclusion has led him to add: "This clearly requires considerable modification of the claims of Owen and Morris that lattice-spacing methods indicate whether constituents had reached thermodynamic equilibrium". In neither investigation was a claim to having established equilibrium conditions made at the lower temperatures—in fact, it is expressly stated by Owen and Sully† in connection with alloys quenched from 350° C. "It is also obvious from the spectra that the alloys have not reached their final state of equilibrium and that they will have to be submitted to further heat-treatment". The true position is, therefore, that, contrary to the classical metallurgical methods, the X-ray method enables a definite statement to be made about the state of equilibrium of the alloys.

Professor Raynor then tabulates the results of Owen and Sully and of Owen and Liu on the $(\alpha + \gamma)/\gamma$ boundary and criticizes us for having represented them in our Fig. 2 by a single curve. Reference to Owen and Sully's first paper‡ would, however, have shown him the following statement (p. 632) "... the γ boundary may have to be moved a little further towards the nickel end of the diagram". In view of this, we felt justified in drawing a single curve as the best representation of the work of Owen and Sully and of Owen and Liu, in the same way that Marsh has drawn a single curve to represent the best result of the many classical investigations of this boundary. and it should be noted that the latter curve represents results which differ by as much as 15% or more at certain temperatures.

This will also serve to answer Raynor's remarks about the comparison of

* *J. Iron Steel Inst.*, 1949, **163**, 132.

† E. A. Owen and A. H. Sully, *Phil. Mag.*, 1941, [vii], **31**, 335.

‡ *Phil. Mag.*, 1938 [vii], **27**, 614.

the discrepancy of 3.7% between two X-ray investigations on iron-nickel, and of 0.5% between two microscopic investigations on copper-germanium. In the former case, the results were published subject to the above-mentioned proviso, whereas we are not aware in the latter of any statement which envisaged the possibility of an error greater than 0.3 at.-% in the first communication, although in the second communication the discrepancy is admitted to be due to a failure to detect precipitated ζ .

To sum up, we feel there is no doubt that, taking the diagram and its associated difficulties as a whole, the X-ray methods have for the first time enabled the position of the phase boundaries to be located with reasonable precision.

We shall now return to Hume-Rothery's survey of the work on the alloys of copper and silver. He begins by referring to the well-known case of the β regions of the copper-zinc and silver-zinc systems, where there is disagreement between the results of the X-ray and the microscopic work on quenched specimens. Both he and Dr. Andrews criticize our statement on p. 153 "that the structure spectra of the constituents indicate whether they have reached thermodynamic equilibrium", and we agree with their criticism to the extent that our statement was given in the wrong place in our paper; it should, of course, have been inserted at the bottom of p. 154 after our conclusion that it is desirable to examine certain alloys in all systems at high temperatures to check the results obtained with quenched specimens. That is to say, if high-temperature work has shown that the work on quenched specimens is trustworthy, the structure spectra taken at room temperature certainly indicate whether they have reached thermodynamic equilibrium, and if high-temperature work shows that work on quenched specimens is unreliable, the same conclusion then applies to the high-temperature photographs.

Dr. Hume-Rothery also states: "It is hardly reasonable to say in one part of the paper that the X-ray films indicate true equilibrium, and then to say later that if only the investigators had known that decomposition had occurred they would have used a high-temperature camera". It is, of course, permissible to point out the mistakes of our earlier work, although in fairness it should be noted that the omission to check the work on quenched specimens in the silver-zinc system by high-temperature work was due to facts expressly stated by Owen and Edmunds* that at that time the vacuum-fibre camera had not been developed and that the high-temperature precision camera technique hitherto employed was not satisfactory in view of the volatility of zinc. It is readily admitted that the decision to employ quenched specimens only, has apparently led to incorrect results in this system, but we do not think that a considered judgment can regard this as a condemnation of the X-ray method as a whole. As we have stated in our paper, high-temperature work must be regarded as an integral part of the X-ray method of determining phase boundaries, so that whether decomposition occurs on quenching or not, quantitative tests can be made to determine whether thermodynamic equilibrium has been set up in the specimens.

It is interesting and instructive also to compare this with the microscopic method in cases where a constituent decomposes on quenching. Neither Dr. Hume-Rothery nor Dr. Andrews is willing to concede that in general such systems are unsuitable for examination by *any* method employing quenched specimens. They support their argument by claiming that the microscope can distinguish to a quite high degree of accuracy between alloys whose structures are of the (α + decomposed β) and wholly decomposed β types, respectively. However, Hume-Rothery points out that the method fails when the amount of α is so small as to be indistinguishable from the finely

* E. A. Owen and I. G. Edmunds, *J. Inst. Metals*, 1938, **63**, 267.

divided α in the "decomposed β ". It was this, of course, we had in mind when we made our statement, since the accurate location of the $(\alpha + \beta)/\beta$ boundary demands the detection of small amounts of original α , and a similar argument applies to the $\beta/(\beta + \gamma)$ boundary.

It is also relevant at this point to quote the remarks of Dr. Gayler in connection with the decomposition of the β phase in the aluminium-zinc system. In the discussion on her paper, she says: * "The writers 'wonder why this method of etching shortly after quenching was not used'. We did use this method at the outset of the investigation, but found that even quenching the alloys into iced water would not always suppress the β -transformation *which is essential if a second phase is to be identified* (our italics). . . . We found that, if a second phase was to be identified before the transformation decomposition took place it was essential to etch at the temperature of quenching." We have some difficulty in reconciling these statements with the claims of Hume-Rothery as to the accuracy of the microscopic method with the technique adopted by him, but whatever is the true position in this connection, it is clear that the method cannot possibly be as accurate as it is claimed to be in cases where no decomposition occurs. There appears to be no escape from the conclusion that high-temperature work is the only satisfactory method of accurately locating phase boundaries in such systems, and that it alone can decide whether the interpretation of the microstructure of quenched specimens is correct.

It is also perhaps worth while to note that while high-temperature X-ray technique is difficult and cannot at the present time be regarded as entirely satisfactory, it would certainly appear to be in better case than high-temperature microscopic technique. The difficulties attending the microscopic examination of a specimen actually at high temperature are formidable, and extensive precautions would have to be adopted to guard the polished surfaces against oxidation and volatilization.

A further point which we should like to raise is the possible acceleration of decomposition after quenching by the surface preparation of the specimen for microscopical examination. We have been unable to find any explicit reference to this possibility in the metallurgical literature, but Mr. Rooksby in his contribution to the discussion states that he encountered an alloy in which a face-centred-cubic high-temperature structure can be successfully quenched-in in a specimen untouched after quenching, but "at the slightest provocation transformation to the hexagonal close-packed structure takes place, and even deeply etched prepared surfaces show this form on X-ray examination. With surfaces quenched from high temperatures, however, X-rays disclose the cubic structure alone." It appears therefore that careful consideration of the problem would be very desirable. It is certainly not impossible that the greater chance of retaining a high-temperature phase in the lump owing to the more sluggish nature of the reactions may be nullified by effects of this sort.

On the general question of the investigation of alloy systems where high-temperature phases decompose on quenching, it is possible to say that if the effects mentioned in the last paragraph are absent, the microscope gives a definite indication of decomposition, whereas the X-ray method using quenched specimens does not; that the latter defect may be remedied by high-temperature X-ray technique; and that the phase boundaries can, in our opinion, only be accurately determined in the present stage of development by the latter method.

Dr. Hume-Rothery then remarks that in the other copper and silver diagrams there is in general very good agreement between the two methods,

* M. L. V. Gayler, *J. Inst. Metals*, 1938, **63**, 146 (discussion).

but it is not quite correct to say that where the solubility diminishes at low temperatures the X-ray results have indicated a "slightly" smaller solubility—at least not on Hume-Rothery's own criterion in the earlier part of his contribution of "slight" and "marked". Thus, the difference of 0.4 at.-% arsenic in the copper-arsenic system at 300° C. between the X-ray work of Mertz and Mathewson and of Owen and his collaborators is to be regarded as "marked", whereas the differences of 0.8 at.-% cadmium in the silver-cadmium system at 300° C., of 1.8 at.-% germanium at 200° C. in the copper-germanium system (later reduced to about 1.3 at.-% by Hume-Rothery, Raynor, Reynolds, and Packer, *J. Inst. Metals*, 1940, **66**, 209), and of about 2.5 at.-% indium in the copper-indium system at 500° C., between the X-ray and microscopical results are apparently to be regarded as "slight". With the exception of the copper-indium system, the X-ray work indicates a smaller solubility. This is generally acknowledged to be due to the tendency of the microscope to give too wide single-phase fields owing to the failure to detect a finely dispersed precipitate at the lower temperatures, and Hume-Rothery agrees that the X-ray results are to be preferred. At the higher temperatures the two methods in general agree more closely, e.g. 0.5–0.6 at.-% germanium in the copper-germanium system at 821° C.; about 0.8–1.0 at.-% gallium in the silver-gallium system between 400 and 600° C.; 0.2–0.3 at.-% indium in the copper-indium system at 715° C.; 0.6 at.-% aluminium at 450° C. to about 0.3–0.4 at.-% at 779° C. in the silver-aluminium system; and 0.6 at.-% gallium at 600° C. to 0.2 at.-% at 914° C. in the copper-gallium system.

In view of this, as stated in the paper, we fail to find sufficient grounds for Hume-Rothery and Raynor's contention that "as the temperature is raised the older methods become relatively more suitable, and the X-ray methods may well be confined to cases where the solubility range is very small or the boundaries nearly vertical". The differences which exist between the two methods at the higher temperatures are believed by Hume-Rothery to be an indication that the microscopical results are to be preferred, since they "involve longer times of annealing and also refer to the part of the lattice-spacing/composition curve where the latter [i.e. X-ray technique] is least certain". The mere fact that the lump specimens have had a longer annealing treatment than the powder specimens is, however, no evidence that equilibrium conditions have been set up in the former, since as we shall show later, a satisfactory method of testing for this is still lacking with the lumps, whereas this is not so for the powder. Also there is no fundamental reason why the lattice-spacing/composition curve should be more inaccurate at the higher temperatures, although we agree that abuse of the X-ray method through lengthy extrapolations may give this impression. The argument advanced by Hume-Rothery also implies that at the higher temperatures the admitted failure of the microscope to detect a finely dispersed precipitate no longer applies, presumably on the grounds that the second phase will in such cases be distributed on a relatively coarse and microscopically visible scale. Whilst this may be true for an alloy containing appreciable quantities of the two phases, in an alloy containing only traces of a second constituent, which is the vital one from the microscopic point of view, would not the requirements of homogeneity demand that it should be distributed as finely as possible, and thus again tend to widen the single-phase fields at the expense of the duplex region? It would seem to us therefore somewhat hasty to conclude that the microscopical results are to be preferred, and there is at least an equal probability that the latter results are in error as it is claimed by Hume-Rothery that the X-ray work is. It would also appear necessary, in each system examined, for the microscopists to state the temperature above which they consider their results reliable.

We are therefore unable to agree that Hume-Rothery's "more comprehensive" review of the results obtained by the two methods, serves only

to emphasize that the conclusions reached in 1942 are substantially unchanged. We are firmly convinced, as stated in our paper, that a considerable change in emphasis is required in this connection.

We may also at this point comment on both Hume-Rothery's and Raynor's complaint that we have omitted to refer to more recent microscopic work which agrees with X-ray work. We feel that we are entitled to ask in this connection why is it that this allegedly satisfactory method of investigation did not achieve these results before? It is true, of course, as mentioned by Professor W. R. D. Jones, that the development of X-ray methods has had the indirect effect of causing an improvement in the technique of the older (microscopic) method, but it appears not altogether too presumptuous to suggest that the fundamental difficulty of the surface preparation of the microscopical specimens and the neglect of satisfactory safeguards to check the composition of the surface layers are such that the microscopists have absolute confidence in their results only when they have obtained agreement with other methods.

We are unable to follow Hume-Rothery's argument when he remarks that the method adopted in microscopical work to ensure that the specimens have reached true equilibrium is the same as that in the X-ray method, and that there is nothing to choose between the two. Surely there is all the difference in the world from a scientific view point between a qualitative and a quantitative method. We also find it somewhat difficult to understand his remarks about the changing parameter in the work of Owen and Rowlands on the copper-arsenic system, since he seems to imply that no allowance for error of measurement should be made. In the work referred to, this allowance was, of course, made, and we cannot accept the new interpretation of the results advanced by Hume-Rothery. But even if in an isolated instance the published lattice spacings had been varying slightly, it would not detract in the slightest from the ability of the X-ray method to deal with this problem. Furthermore, the increased accuracy which may be confidently looked forward to in the measurement of lattice parameters will further improve the X-ray method, but we cannot envisage any significant improvement in the immediate future in the acuity of the human eye.

With regard to our criticism of the microscopic method, Hume-Rothery remarks that our argument that the difficulties should lead to a distrust of microscopical metallography in general "is as unreasonable as it would be to suggest that the X-ray methods are unreliable because in some cases two phases give rise to diffraction spectra which are closely similar or have overlapping lines". It is, however, not so unreasonable as Hume-Rothery suggests, for the simple reason that our objections apply to practically every specimen examined microscopically, whereas the possibility he visualizes in the X-ray case is the rare exception rather than the rule.

We do not imply that equilibrium diagrams have been based on the microscopic examination of unetched alloys, and the references were given in our paper simply to point out specific examples of the examination of unetched specimens; no mention was made in the paper of their use for the determination of equilibrium diagrams. Dr. Hume-Rothery and Professor Raynor have gone into detail to explain the position in this connection, but as will appear from the following quotations from the literature it is worth noting that there does not always appear to be conclusive evidence that the etched surfaces by means of which the results obtained on unetched surfaces are tested, are themselves free from the effects of surface preparation.

Professor Chaudron* states: "Mechanical polishing produces in addition to a very heavily cold-worked surface layer a more or less deep distortion of

* G. Chaudron, *J. Inst. Metals*, 1949-50, **76**, 10.

the crystal structure. Moreover, mechanically polished metal is covered with an oxide film. In short, it may be said that two skins are formed: the one structural, which is more or less deep, and the other chemical, consisting of an oxide film. These two skins often mask the real surface properties and even the properties of the metal in massive form." Also Maddin and Hibbard* state: "In the present investigations a minimum of 0.125 in. was removed after mechanical cutting and polishing and yet a disturbed structure was apparent, when investigated with directed characteristic radiation. . . ."

We regret that our statement on p. 149 that whereas the X-ray method provides a safeguard against contamination "no such tests are available in the microscopical method", is not sufficiently clear; the difficulty has arisen through a too severe economy of words. As Hume-Rothery remarks, there are numerous statements in published papers that the actual specimens used for microscopical examination have been submitted to chemical analysis, and we are perfectly satisfied that the *overall* composition of the specimen is beyond reproach. What we had in mind, however, was that the position with regard to the actual surface examined microscopically may not be so satisfactory. Thus, while a specimen found on analysis to contain, say, 99.99% total metal and 0.01% absorbed gases, &c., may on the whole be considered free from contamination, this would be by no means true of the microscopically examined surface layers if the impurity were segregated there, as is not altogether unlikely. It appears to us that the volume of material examined microscopically is so small a fraction of the total volume analysed chemically that there can be no certainty in general that these regions are free from contamination. Moreover, even in an uncontaminated specimen, the actual composition of the surface layers would seem to be commonly in doubt, since there does not always appear to be sufficient justification for the assumption that it is the same as the average composition of the whole specimen. For instance, Hume-Rothery and Raynor† state: "If suitable sections are examined, the microscopic method provides a satisfactory safeguard against errors due to uneven composition of the specimen. Thus with alloys of the α/β brass type, difference of composition of the order 0.2 at.-% can readily be detected microscopically, and, since the actual specimen examined can be used for analysis, the method is one in which the composition can be kept under accurate control." Since the estimate of 0.2 at.-% in the α/β brass alloys implies that in other systems the agreement is not so good, we would suggest that the safeguard is not so satisfactory as is commonly supposed, and even if our inference is not true and the figure of 0.2 at.-% applies to all systems, in many diagrams it may be somewhat precipitate to conclude that phase boundaries have been determined by the microscopic method to 0.1 at.-% and sometimes better. Hume-Rothery and Raynor, in the paper referred to above, conclude that in accurate X-ray work, nothing except the analysis of the filings in their final state is satisfactory. We suggest that this conclusion ought to be applied also to the microscopical specimen, and that nothing except the analysis of the actual surfaces in their final state is satisfactory. We may add also that in many cases (for example, most of our work at Bangor) the lattice-spacing method does enable the actual composition of the irradiated sample to be determined, but we have not yet come across an instance of microscopic work where the precaution described above has been adopted.

With regard to the relative times of annealing of filings and material in

* R. Maddin and W. R. Hibbard, Jr., *Trans. Amer. Inst. Min. Met. Eng.* (in *J. Metals*), 1949, 185, 700.

† W. Hume-Rothery and G. V. Raynor, *J. Sci. Instruments*, 1941, 18, 74.

lump form, Hume-Rothery suggests that our conclusion that equilibrium is attained more rapidly in filings is, except for volatile metals, the result of our having been concerned mainly with alloys in which precipitation occurs on re-annealing. We think that this concluding phrase would express the common experience of everyone concerned with equilibrium-diagram determinations, for the simple reason that increasing solubility with decreasing temperature is the exception rather than the rule. It appears to us therefore to provide ample justification for our conclusion.

The example discussed by Hume-Rothery in which reactions are expected to occur between individual particles of a mass of filings is, in our opinion, an instance of the misuse of the X-ray method rather than a well-sustained argument that the annealing times of filings are longer than those of the lump. It is essential to ensure that the ingot is in a satisfactory condition before the final sample of filings is taken from it, and as we have indicated in the earlier part of our paper extensive precautions are taken in this connection. In the case of a solubility line where the solubility increases with decreasing temperature, it is important to anneal the ingots of two-phase alloys to ensure equilibrium either at the temperature corresponding to the actual maximum solubility or else at the lowest temperature in the range in which the solid-solubility line is to be determined. It is then only necessary to remove the lattice distortion present in the filings, and to cause precipitation of the second phase by annealing to equilibrium at different temperatures, no reactions between the individual particles are required to occur, and the contingency visualized by Hume-Rothery does not arise.

Dr. Hume-Rothery concludes that "everything is to be gained by combining the microscopical and X-ray methods". We would again emphasize that we are not categorically opposed to this view, but summing up our criticisms regarding the application of the micrographic method to the *precise* determination of phase boundaries, the following conclusions seem unavoidable: (1) No satisfactory tests have been proposed to decide whether equilibrium has been set up in the lump specimens; (2) there is uncertainty in the actual chemical composition of the surfaces examined microscopically; (3) no satisfactory means of deciding whether the prepared or the etched surfaces are free from the effects of the polishing processes have been suggested (it is not enough to state that the microscopists are aware of this difficulty); (4) at the higher temperatures no satisfactory evidence is forthcoming that the microscope is still not subject to the danger of being unable to detect small quantities of a second phase, as is admitted to be the case at the lower temperatures.

In view of our detailed replies to Hume-Rothery's criticisms and the fact that none of the above objections were mentioned at the 1942 conference, we cannot agree with Hume-Rothery's emphatic statement "that no evidence has been produced which alters the general conclusion reached in 1942". It appears to us that a modification is required in the general impression created by this Conference and particularly by Hume-Rothery and Raynor's earlier paper, viz. that although the two methods should be used in conjunction, the microscope is the final arbiter in the accurate determination of phase boundaries except at unspecified lower temperatures. It also appears to us that, in general, microscopical work in phase-boundary determination can be accepted with absolute certainty only when it has been confirmed by an independent method, and we wish to re-emphasize the conclusion arrived at in our paper, viz. that in general the main emphasis should be on the X-ray powder method, *over the whole temperature range*, with other methods requiring lump specimens as subsidiary to it.

We now return to the more general points considered by Professor Raynor. With regard to the composition of the filings, our argument was developed to

show that the earlier statement of Hume-Rothery and Raynor (1941) that in accurate work only chemical analysis of the final sample is satisfactory, is not justified. In a great number of cases, contamination can be tested for, and the composition determined by the methods indicated in our paper with at least the same degree of accuracy as that obtained by actual analysis, and in these, therefore, the latter technique is not required. Of course, there will be certain instances, such as silver-aluminium cited by Raynor, where the lattice spacings are constant over a range of composition and segregation cannot be tested for by this method either, but we can hardly believe that our remarks could have led him so far astray as to think that we have proposed discarding chemical analysis altogether. We may remind Professor Raynor also that our experience has included work on the not altogether well-behaved systems copper-arsenic, silver-arsenic, and iron-nickel.

We agree with the statements that the fact that contamination effects have been absent in the Bangor experiments does not mean that they cannot be encountered with other materials, and that the extent to which contamination may affect X-ray results depends entirely on the alloy system concerned. Each system must be regarded as a problem in itself, and it is incorrect for Raynor to imply that tests for contamination are omitted because the errors do not show up with gold alloys.

We find it a little difficult to reconcile Raynor's statement that with certain iron alloys, a "speck of soot" might convert some of the filings into an austenitic steel with his claim that with iron little effect is to be expected at low temperatures even if oxygen, carbon, and nitrogen are present.

With regard to our experiments with aluminium on the effect of grain-size, the results, contrary to the experience of the Oxford workers, were quite consistent, and gave a variation in the opposite direction to that which would be expected from silicon contamination. However, no chemical analysis was made, and as further experiments are at present in progress on this phenomenon, it is premature to arrive at a definite conclusion as to the explanation.

We still think it reasonable to infer that if the pure metals do not show contamination this is also the case with alloys prepared by the same technique, in spite of the magnesium-cadmium alloys mentioned by Raynor. For instance, aluminium-magnesium alloys are less reactive than is magnesium itself. But the important point which Raynor omits to mention is that we do not rely on this inference when dealing with alloy systems. In the very next sentence to that mentioned by him we specifically refer to the technique which is adopted to test for contamination or change of composition in such cases. In any event, it appears to us that the effects described by Raynor where the composition of the alloy matrix is altered by the penetration of the nitride phase into the crystals along crystallographic planes would be more readily detected by X-ray methods than by any other, unless the actual surface layers were chemically analysed, which does not appear to be common practice with microscopists.

To sum up this section, we would be prepared to agree that the composition of filings taken from an ordinary metallurgical specimen would be suspect without actual chemical analysis, but in our opinion, insufficient attention has been paid by Raynor to the extensive precautions which are adopted to secure a satisfactory ingot before the final samples of filings are taken from it. We are satisfied that with careful work the fears expressed earlier by Hume-Rothery and Raynor in this connection are much exaggerated, and that in the cases where they do exist they may be satisfactorily tested for and remedied.

The difficulty which Raynor mentions with regard to volatilization may be overcome by the simple expedient of dispensing with the use of a silica or

glass tube altogether and employing another refractory material such as alumina.

Professor Raynor considers that our suggestion that strain-induced precipitation during preparation may give abnormally low solubility values, is improbable. We must admit that in view of the oft-repeated claims of the microscopists about the sensitivity of the microscopic method we gave the microscope the credit of being able to detect any precipitated particles which may exist, and if this is so, it would undoubtedly give narrower single-phase fields as we suggested. Apparently, however, many cases exist where the microscope is unable to give a correct and unambiguous interpretation of the state of a specimen as it actually is at the moment of examination.

In his last paragraph Raynor remarks "any such attempted generalization is useless". May we now assume that this applies to the generalizations on the X-ray method, of which he is part author, published in 1941?

In reply to Dr. Andrews we must re-affirm that the point we made was that if an equilibrium diagram is investigated either by the X-ray powder method alone or by classical methods alone, the former in general is more likely to be correct, and we see no reason to change this view. If both methods are used we still maintain that in general greater weight should be attached to the X-ray results.

As regards the comments on the copper-zinc and silver-zinc systems, we must refer Dr. Andrews to our reply to Hume-Rothery on this question. He will notice also that at the bottom of p. 153 we point out that the procedure outlined involves the assumption that the condition of the alloy at a given temperature of annealing is retained by quenching, and on p. 154 we ourselves stated that the boundaries of the β -region of the copper-zinc and silver-zinc systems appear to have been incorrectly located by the X-ray method, owing to decomposition on quenching.

Dr. Andrews is also unwilling to concede that in general this admitted weakness of the method of quenching as applied to the X-ray method is common to the classical methods also, and we must again refer him to our reply to Hume-Rothery on this point. His statement, in connection with the silver-aluminium alloy, that "the original grains of ζ are quite readily distinguishable from the background which may contain ζ as a decomposition product of β " must be qualified in the way indicated in Hume-Rothery's statement, by the remark that this is only true provided the amount of original ζ is sufficiently great and that it is not distributed on a sub-microscopic scale. With these last two provisos we accept his statement that "the appearance of the microstructure of a phase which has decomposed on quenching is quite distinctive and very different from the appearance of samples where two phases have been in equilibrium at the temperature from which the specimen has been quenched, and no decomposition has occurred", and presume that this is applicable to all alloy systems and not merely to the examples quoted by him. But in view of the exceptions mentioned, and as we have explained in more detail in our reply to Hume-Rothery, we are of the opinion that claims to have accurately determined an equilibrium diagram by the microscopic method using quenched specimens alone must be substantiated by high-temperature work before they can be accepted with confidence, and that this confirmation is not merely "acceptable" but essential.

Some of the points raised by Dr. Andrews on the silver-gallium system have been dealt with in our reply to Hume-Rothery, and we must apologize for not having included the α -solid solubility line determined by him and Hume-Rothery in our Fig. 7. We are glad to see the estimate of temperature above which the microscopic method is regarded by Dr. Andrews as being satisfactory, as we have suggested this would be very desirable in all such cases.

Dr. Andrews also apparently fails to appreciate that the point at 211°C .

given in our Fig. 7 and determined from his and Hume-Rothery's lattice parameter of a two-phase alloy at 211°C . was included with the purpose of showing the almost exact agreement of the results of two independent X-ray investigations, one at Bangor and the other at Oxford, whereas there is serious disagreement in this region between the two microscopical investigations made at Oxford. As stated more fully in our reply to Hume-Rothery (p. 700), the point at 211°C . in our Fig. 7, was incorrectly deduced by us as 11.0 at.-% gallium instead of 11.8 at.-%. The figures quoted by Dr. Andrews now become 0.5% at the peritectic temperature, 0.6% at the transformation temperature, and about 0.4% at 200°C . The agreement at the lower temperatures is therefore much better.

Dr. Andrews' reply to the question we asked in introducing the paper does not seem to be entirely satisfactory, since the slopes of the two curves are practically identical in the temperature range 615° – 382°C ., and also at about 300°C . It is only between 382° and 300°C . that the solubility of gallium diminishes more rapidly according to Hume-Rothery and Andrews's results, whilst below about 300°C . the extrapolated curve of Owen and Rowlands actually indicates the reverse may be true.

We may also remark that there is a somewhat unnecessary and rather confusing interchange in phraseology in two of Andrews' statements in this paragraph. In the first he says "The phase boundary (i.e. Hume-Rothery and Andrews) is to the gallium-rich side of that of Owen and Rowlands for the temperature range 615° – 300°C . which was the lowest temperature at which these authors determined the boundary". Later on we find "Their phase boundary (i.e. Owen and Morris's) over the temperature range in question is now shown to the silver-rich side of ours". It would seem to be a little clearer and to throw the adjusted curve of Owen and Morris into proper perspective if the operative word "now" were replaced by "still" in this last sentence, and as may be seen from Fig. A, the change from Owen and Rowlands is very slight over the whole temperature range.

Dr. Andrews remarks "The limitations of the method of using lattice-parameter/composition curves should be fully appreciated and many of these limitations have been fully stressed elsewhere". The only limitation of which we are aware is the one stated in our paper, viz. that the final accuracy depends on the slope of the lattice-parameter/composition curve.

With regard to the case discussed by Andrews of first an increase in solubility with decreasing temperature and then a decrease in solubility, the correct conclusion is not that "The same difficulties *might* (our italics)" but that "The same difficulties *will* apply to any method of investigation in this region", and the X-ray method does not suffer by comparison with other methods in this connection.

We are glad to receive Dr. Andrews's assurance that the limitations of the metallographic methods to which we directed attention are well-known amongst the investigators who employ them. The case of the austenitic steels mentioned is particularly interesting and would seem to be a further instance of these limitations rather than the reverse. For example, the statement that "On the other hand, any α originally present is readily distinguishable" must be qualified by the words "provided it also is not distributed on a sub-microscopic scale", and it would certainly seem more satisfactory to employ a method which gives positive evidence as to the actual condition of a specimen rather than to rely in such cases on the negative attribute of the microscope of inability to detect such effects. We should be interested to know, for instance, whether the microscope would give a "substantially correct representation" of the condition of alloys which at the quenching temperature consisted of (α + small amounts of γ) and (γ + small of amounts of α).

We agree with the remarks contained in the last paragraph of Dr. Andrews's contribution, and would suggest that increasing use be made of the X-ray method in correlating particular aspects of the structure of alloys with desirable mechanical and other properties. As Bragg * has pointed out "There is a range of dimensions between the smallest structure visible under the microscope and the scale of the atomic pattern which is actually more extensive than the range between coarse structures visible to the naked eye and those which can be seen under the highest powers. X-ray analysis conveniently covers the lower range. It takes over just where the microscope can no longer be used, and carries us down to the scale of the atomic structure itself. Further, the structures which are found on the scale between 10^{-4} and 10^{-8} cm. are probably of as much importance to the mechanical properties of the metal as the structures visible under the microscope".

We are much interested in Dr. Christian's calculations on the sensitivities of the two methods, which appear to establish that in many cases the microscopic method does not suffer in this respect by comparison with the X-ray method, and in the inference which is to be drawn from this, viz. that the same conclusion will apply to their relative accuracy in phase-boundary determination. We would like to comment first on his statement that "The final accuracy (in the X-ray method) of the boundary is limited by the accuracy of the chemical analysis of the alloys used to determine the spacing curve". The correct statement here is that the accuracy is limited by the accuracy with which the chemical composition of the irradiated specimens is known, and there is no *a priori* necessity to specify chemical analysis. For instance, in much of our own work at Bangor, the composition of the final specimen is determined, not by actual analysis, but firstly by careful control during preparation of the ingots, and secondly by lattice-parameter tests on the samples of filings prepared from them. As stated in our paper, the actual composition of the ingots was found by chemical analysis to agree in our earlier work to within 0.05 wt.-% of the estimated value for both volatile and non-volatile constituents, and since improvements in our technique can reasonably be expected to have occurred since then and no ingot is regarded as satisfactory until its weight agrees to within a few parts in ten thousand with that of the ingredients used to make it, the composition of the ingot as a whole is known to a somewhat better degree of accuracy than the 0.1 wt.-%, which Dr. Christian considers applicable to actual analysis figures. Secondly, the degree of homogeneity of the ingot is determined by taking filings from different portions of it, as indicated in other papers from this laboratory, the sensitivity of this test, of course, depending upon the rate of change of parameter with composition in the particular alloy system concerned. This method has the advantage, therefore, that the accuracy with which the composition of the specimen is known is automatically adjusted to be the same as that with which the boundary may be determined from the lattice-parameter/composition curve, since as Dr. Christian points out, the use of a method with a high sensitivity on the one co-ordinate will not lead to a greater accuracy in the boundary unless there is a corresponding increase in the accuracy on the other.

Next we may comment on Dr. Christian's estimate of an accuracy of 1 in 30,000 in an individual determination of lattice parameters. It is true that this has been a commonly accepted estimate for some considerable time, and probably only a few of those who have used the lattice-parameter method for phase-boundary determination have attained an accuracy greater than this. Nevertheless, since we are mainly concerned with the potentialities of the X-ray method in equilibrium-diagram work, it should be mentioned that considerable

* W. L. Bragg, *J. Iron Steel Inst.*, 1940, **141**, 66p.

improvements have taken place recently in X-ray technique and it is now fairly commonplace to determine lattice parameters with a relative accuracy of 1 in 50,000 or even better. For instance, Thomas * has described a method which in many cases will give an accuracy of 1 in 100,000, whilst the technique developed by Straumanis † has been claimed to give an accuracy in some cases of more than 1 in 200,000, even with crystals of lower symmetry. It is clear, therefore, that these figures would produce considerable changes in the values of Δc calculated by Dr. Christian, the important point being that the use of these improved X-ray techniques is warranted by the comparable increase in accuracy with which the composition of the specimen can be determined.

Turning now to the microscopic method, we agree with Dr. Christian that as regards sensitivity it does not suffer by comparison with the X-ray method in many cases. It does not follow, however, that this conclusion holds automatically for their relative accuracies. For instance, in what seems to be a fairly favourable case, Hume-Rothery and Raynor state that the microscope is able to detect variations in composition in a microscopic section of only 0.2 at.-%, and many cases will undoubtedly exist where this figure is appreciably higher. It may not be justifiable, therefore, to assume that the composition of the surface layers, which after all is the vital point in the microscopic method, is known to the 0.1 at.-% accuracy which applies to the overall composition of the specimen. When possible effects due to surface preparation are also considered, it would seem, therefore, somewhat optimistic to conclude that the accuracy of phase-boundary determination by the microscopic method is the 0.1 at.-% claimed by Dr. Christian, and we suggest that this may be partly the explanation of the discrepancies which are noted by him.

We agree with him that greater difficulties are encountered in preventing contamination of filings of the more reactive alloys, and he is mistaken in inferring that we have concluded that contamination can never occur. The discussion given in our paper was intended to show that tests can be and are applied to deal with this problem, and we believe that such tests are essential before the X-ray method can be regarded as being really satisfactory. Dr. Christian seems to be so preoccupied by chemical analysis that he has apparently failed to see the significance of these tests, although his statements are indirectly an admission that they would be superior to analysis in the detection of the small amounts of gaseous impurities which he mentions.

The case of the cobalt-rich alloys discussed by Dr. Christian is very interesting, especially since, from his remarks, it would appear that the microscopic method is incapable of giving any information at all about the phenomena involved; they would probably have still remained undiscovered and many fictitious phase boundaries advanced if X-ray analysis had not been available to investigate the problem.

We wish to thank Mr. Goldschmidt for his very interesting comments on our paper. We are glad that he has reached the same conclusions as ourselves regarding the more rapid attainment of equilibrium in the powder, and this fact now appears to be established. It is also comforting that Mr. Goldschmidt believes that "For true equilibrium investigations and rapid surveys, the powder method is certainly supreme". The "difficulty arising where correlation with practical properties such as hardness, tensile strength, &c., is required" is, of course, appreciated, but, strictly speaking, this point is not relevant in the investigation of equilibrium diagrams as such, with which we were primarily concerned in our paper. We agree, however, with Mr.

* D. E. Thomas, *J. Sci. Instruments*, 1948, 25, 440.

† M. E. Straumanis, *J. Appl. Physics*, 1949, 20, 726.

Goldschmidt's suggestion as to the best compromise which can be adopted in such cases, and we are very interested in the technique which he describes in this connection.

We are sorry that Mr. Goldschmidt has understood us to state that certain systems are unsuitable for examination by any other method whether on powders or lump, simply because decomposition occurs in quenched filings. What we meant was that if decomposition occurs also in the lump they will be unsuitable for room-temperature investigation. We certainly agree that in the absence of surface preparation there is a better chance of retaining a high-temperature phase in the lump than in the powder, but should decomposition still occur, we have no doubt that Mr. Goldschmidt will agree with our contention and that high-temperature work provides the only really satisfactory answer to the problem.

We are also glad that Mr. Goldschmidt agrees that the surface preparation of block specimens presents a fundamental difficulty, and we must thank him for quoting the examples of phase transformations produced by it which he has encountered. With regard to etching techniques to remove the cold-worked layer for X-ray test on the block, far from rejecting them outright as suggested by Mr. Goldschmidt, we offered no comment at all on this possibility, since the feasibility of such methods can only be tested by experiment. Electrolytic etching would certainly appear promising in this connection.

The variations in the parameter of individual crystals in a polycrystalline aggregate which we mentioned and to which Mr. Goldschmidt refers were measured not by the microbeam technique but by a method developed at Bangor, a full account of which will be published elsewhere. Mr. Goldschmidt will no doubt be interested to learn that his "daring" suggestion that in a polycrystalline mass ideally perfect equilibrium can theoretically never be attained is in agreement with our own findings and conclusions.

We are sorry that our discussion of the powder technique dealt only with the preparation and heat-treatment of filings. The X-ray method, of course, is applicable to powder obtained by any method, such as the grinding and drilling mentioned by Mr. Goldschmidt, and the same tests for contamination, &c., may be carried out equally well. Mr. Cantrell, in this discussion, has indicated a method employing a metal-bonded diamond hand-hone which is claimed to overcome contamination difficulties, and the use of which would, we imagine, reduce the most hard and brittle metal to powder. We have had an opportunity of testing the hone which he mentions, and have found it eminently suitable for the purpose.

The choice of a suitable container for the heat-treatment of the powder is, of course, sometimes difficult, and the development of a wider range of refractory materials is greatly to be desired. We regret that it is not possible at present to specify a refractory which is suitable for all alloys and under all conditions, but alumina, beryllia, thoria, or magnesia containers would appear to be satisfactory in most cases. One difficulty encountered in the high-temperature heat-treatment of powders is the sintering which occasionally occurs. In the cases we have met at Bangor this can be successfully overcome by mixing the powder with a coarser grade of alumina and sieving off the former after heat-treatment. We have not ourselves employed sealed-off evacuated alumina tubes as envisaged by Mr. Goldschmidt, but have had to use a continuously evacuated furnace or one employing an inert atmosphere. The latter is often more convenient where rapid quenching is desired.

Mr. Goldschmidt is, of course, correct when he states that our method of testing for contamination mainly refers to the case of substitutional solid solutions, and as we have stated in our reply to Professor Raynor we did not mean that this method can be applied universally, to the complete exclusion of chemical analysis. There will certainly be cases where the latter technique

will have to be employed, although the greater accuracy now attainable in lattice-parameter measurement can confidently be expected to lead to still more accurate phase-boundary determination, even in cases of two elements of similar atomic size, as well as to a reduction in the number of cases where actual analysis is essential.

With regard to the technique of precision lattice-spacing measurement, our experience in the main has been that film viewing by eye is entirely satisfactory provided that due care is taken in the design of the slit system to produce lines with a symmetrical intensity distribution. The use of the microphotometer has usually been reserved for the measurement of diffuse lines such as will not arise in precision lattice-spacing determination.

We are much interested in Mr. Goldschmidt's remarks on the "disappearing-phase method" and in the technique employed by him to increase the visibility of a weak second phase. We agree that this method might prove in some cases to be more sensitive than the lattice-spacing method, but its disadvantage from our point of view in phase-boundary determination is that the actual composition of the two-phase alloy must be known. One of the strongest points in favour of the lattice-spacing method is that the composition of the two-phase alloys is not at all critical.

We agree with Mr. Goldschmidt that the word "desirability" should be modified in our statement at the bottom of p. 154, and that this should now read "Whatever method of investigation is used the work done by the X-ray method on these two systems points, therefore, to the *necessity* of examining certain alloys in all systems at high temperatures to check the results obtained with quenched specimens". We also agree that a complicating factor with the high-temperature X-ray camera, with which we are also faced, is the necessity of deciding the minimum time for which the specimen ought to be held at the high temperature before equilibrium can be assumed and the photograph taken. The only answer appears to be to make more such cameras available to carry out more extensive investigations at high temperatures.

We wish to thank Mr. Rooksby for his remarks and for the concise summary he has made of the main points of our argument, which does not seem to require any further reply.

Professor W. R. D. Jones's remarks are interesting. There is one point, however, in his contribution which requires reply. He says: "... the X-ray workers ... have been inclined to consider that a phase boundary could be established by using a very much smaller number of alloys than that considered desirable by those using the older method". The number of alloys considered desirable by the microscopists in *their* method has nothing whatever to do with the number required by the X-ray method. The other points which he makes are dealt with elsewhere in our reply and no detailed comment on them therefore seems necessary.

DISCUSSION ON THE PAPER BY MR. S. J. CARLILE AND DR. W. HUME-ROTHERY: "A NOTE ON THE EFFECT OF NITROGEN ON THE STRUCTURES OF CERTAIN ALLOYS OF CHROMIUM AND MANGANESE, AND ON THE EXISTENCE OF AN INTERMEDIATE NITRIDE PHASE."

(*J. Inst. Metals*, this vol., p. 195.)

DR. H. K. HARDY,* M.Sc., A.I.M. (Member): The authors' conclusion is "The work described above shows conclusively that the chromium-manganese alloys concerned possess an extraordinary affinity for nitrogen, and that even though the pressure of nitrogen is extremely low they may be entirely converted into a nitride phase which is not chromium nitride. It is feared that this characteristic will prevent alloys with a chromium-manganese base from being suitable for use at high temperatures."

Large absorption of nitrogen occurred under the conditions of Carlile and Hume-Rothery's experiments, where the partial pressures of nitrogen and oxygen would be extremely low owing to their relatively slow diffusion through the refractory tubes in which the specimens were sealed for heat-treatment. It would be of interest to know whether they have any experience of their alloys heat-treated in air, that is under conditions of relatively high partial pressures of oxygen and nitrogen.

I have not studied chromium-manganese alloys of the type investigated, but chromium-base alloys exposed to air at high temperatures in the solid state normally form a thick and usually adherent layer of oxide. The exact degree of adherence and protection due to the oxide film, and its rate of growth, are a function of the alloying elements present, and there is little evidence of nitrogen absorption. On the other hand, alloys exposed under conditions of low partial pressures of oxygen and nitrogen, show sub-scales of oxide and particles of nitride precipitated within the metal mass (see Figs. A and B, Plate CVIII).

This difference in behaviour with different partial pressures may be explained by considering the variation of reaction rates with concentration. Growth of the chromium oxide film at the metal surface occurs very rapidly under conditions of high partial pressure of oxygen. Diffusion of oxygen into the metal from this film is to be expected, but the growth of the film is probably by outward diffusion of chromium ions and the rate of oxidation is much reduced as the film thickens. This oxide barrier may also be expected greatly to hinder any nitrogen absorption. The concentration of oxygen at low partial pressures may be insufficient to nucleate stable films at the metal surface, or the rate of nucleation may be so slow that the reaction products are dissolved, allowing the oxygen to diffuse into the metal. No continuous film of chromium oxide is to be expected under these conditions, so that nitrogen

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absorption may occur unhindered. Whether the nitride is now formed at the surface or internally will be a function of the nitrogen partial pressure. Precipitation of nitride within the metal will occur when the nitrogen content has been increased above the solubility limit and where a stable nucleus can be formed most easily.

The authors' conditions, which involved very low partial pressures, are thus seen to be ideal for internal nitriding. Their experiences of heat-treatment under conditions of high partial pressure of oxygen would be very valuable. It would enable them to decide whether their chromium-manganese alloys differ significantly from other chromium-base alloys, where failure by internal nitriding when heated in air at atmospheric pressures may be considered extremely improbable.

DR. W. HUME-ROTHERY and MR. S. J. CARLILE (*in reply*): We thank Dr. Hardy for his interesting communication. The work described in the paper has shown that the chromium-manganese alloys concerned are readily nitrified when the pressure of nitrogen is extremely low. Further work has also proved that similar nitriding occurs when the alloys are heated in nitrogen of commercial purity at atmospheric pressure. We have no experience of the behaviour of the alloys in the presence of air, and we agree with Dr. Hardy that it is possible that a protective oxide film might be formed. If Dr. Hardy can establish that this is so we shall be extremely pleased, because it will mean that the alloys may be of practical as well as of theoretical interest.

DR. A. H. SULLY,* M.Sc., F.I.M. (Member), and MR. T. J. HEAL,† B.Sc.: We are extremely interested in the effects of nitrogen on chromium-rich alloys and have devoted some attention to the nature of the nitrogen-rich phase formed in various alloys. Although we have encountered the phenomenon to which the authors refer, of progressive nitrogen pick-up at low partial pressures of nitrogen, we have not found it troublesome during the heat-treatment of the chromium alloys with which we have been concerned, since the contamination is readily avoided by heat-treatment in a slow stream of dry hydrogen.

We have, however, studied the interaction of chromium alloys and nitrogen at higher partial pressures of nitrogen, in particular the structures found in chromium alloys after melting in conditions in which air is not rigorously excluded. Fig. C (Plate CIX) illustrates the typical appearance of a chromium ingot cast after melting in air in an indirect-arc furnace. Analysis of this material after melting showed that it contained 2.05% nitrogen, and the structure shows large quantities of a nitrogen-rich phase as well as a considerable quantity of oxide. Both chromium-cobalt and chromium-manganese alloys, containing up to 30% of cobalt or manganese, exhibit similar structures after melting in air. The quantity of nitrogen-rich phase present in these alloys is quite large and diffraction lines from this phase are clearly visible on X-ray photographs. We have found that the nitride phase has the same structure whether it occurs in chromium or in its alloys with cobalt or manganese within the above limits of composition. Here our results are at variance with those of Carlile and Hume-Rothery, who say that the nitride formed in chromium-manganese alloys is not a chromium-nitrogen phase but is a new substance.

We suggest that this impression results from a misinterpretation of the X-ray photograph, the measurements of which are given in Table I (p. 199) of the paper. It will be demonstrated that this pattern may be interpreted

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as comprising a mixture of lines from a body-centred cubic structure (chromium with manganese in solid solution), and a close-packed hexagonal structure corresponding to the structure of the chromium nitride Cr_2N according to Blix.*

TABLE A.

Bragg Angle from Carlile and Hume-Rothery's Table I	Assumed Values of Miller Indices	Radiation	Calculated Lattice Parameter, kX.	Observed Intensity	Expected Intensity.
76.25°	(211)	CrK α	2.881	s	s
52.69°	(200)	CrK α	2.880	m	m
34.43°	(110)	CrK α	2.857	s	s
62.31°	(211)	CrK β	2.879	w	w
30.99°	(110)	CrK β	2.860	w	w

In Table A we give the angles for five lines taken from the authors' Table I, the Miller indices for these lines assuming them to be derived from a body-centred cubic lattice, the radiation (α or β), and the lattice-parameter values calculated from these assumptions. The observed intensities and the estimated intensities of these lines are also shown.

TABLE B.

Bragg Angle from Carlile and Hume-Rothery's Table I	Hexagonal Indices and Radiation	Calculated Angle for Unit Cell of Dimensions: $a = 2.700 \text{ kX.}$, $c = 4.403 \text{ kX.}$	Intensity According to Carlile and Hume-Rothery	Intensity According to Blix *
26.67°	(100) β	26.4	vw	vw
28.66°	(002) β	28.2	w	vw
29.52°	(100) α	29.3	m	m
30.51°	(101) β	30.3	m	m
31.77°	(002) α	31.3	m	m
33.85°	(101) α	33.6	s	s
41.14°	(102) β	40.5	vw	w
45.79°	(102) α	45.5	m	m
50.41°	(110) β	50.4	vw	w
57.35°	(103) β	57.1	w	w
57.84°	(110) α	58.0	s	s
64.83°	(112) β	64.7	w	w
67.37°	(103) α	67.0	s	s
83°	(112) α	83.6	m	s

The calculated lattice parameters all lie within the range 2.857–2.881 kX. and agree very well at the high-angle end of the film within limits of 2.879 and 2.881 kX., which it may be noted is approximately the value for chromium containing manganese in solid solution.† The intensity values also agree well with those to be expected. The (200) β line, which does not appear, will be appreciably weaker than the (211) β and (110) β lines which are detected as

* R. Blix, *Z. physikal. Chem.*, 1929, [B], 3, 229.

† S. J. Carlile, J. W. Christian, and W. Hume-Rothery, *J. Inst. Metals*, 1949–50, 76, 169.

weak lines. There can be little doubt that this group of five lines can be accounted for by diffraction from a body-centred cubic lattice, and it is suggested, on the basis of this and the following evidence, that in spite of the uniform appearance of the nitrided specimen of the alloy, it still contained unnitrified metal.

The remaining lines listed by the authors in their Table I conform fairly well to a close-packed hexagonal lattice with $a = 2.700$, $c = 4.403$ kX., and c/a 1.631. Table B lists the remaining lines of the authors' pattern, the assigned Miller indices for a hexagonal lattice, the radiation, and the angles at which these reflections should occur, calculated for a unit cell of the above lattice constants.

The extent of the agreement leaves little doubt about the correctness of the fit to an hexagonal structure, although progressive deviations between the values occur along the film from high to low Bragg angles owing perhaps

TABLE C.

Hexagonal Indices and Radiation	d from Carlile and Hume-Rothery's Values, kX.	Intensity	d , kX., for Lines from Air-Melted :			d for Cr_2N , kX. (Blix)
			Cr-30% Mn Alloy	Cr-10% Co Alloy	Cr	
(100) β	2.54	vw	2.61
(002) β	2.38	w	2.43
(100) α	2.32	m	2.34	2.35	2.36	2.38
(101) β	2.25	m	2.26	2.28	2.29	2.31
(002) α	2.17	m	2.17	*	*	2.22
(101) α	2.05	s	2.06	2.07	2.08	2.11
(102) β	1.74	vw	1.78
(102) α	1.59	m	1.60	1.61	1.62	1.62
(110) β	1.48	vw	1.51
(103) β	1.36	w	1.37
(110) α	1.35	s	1.36	1.37	1.38	1.369
(112) β	1.26	w	1.281
(103) α	1.23	s	1.24	1.25	1.26	1.253
(112) α	1.151	m	1.15	1.15	1.15	1.165

* Coincides with body-centred (110) β line at $d = 2.207$ kX.

to film shrinkage, absorption, or other factors. The only line of any intensity not observed is a doublet from the (200) plane which is probably overlapped by the (211) α doublet from the body-centred phase.

Blix † assigns to the hexagonal Cr_2N phase a range of lattice constants from $a = 2.747$, $c = 4.439$ kX., and c/a 1.616, to $a = 2.770$, $c = 4.474$ kX., and c/a 1.616. The value given above is somewhat outside this range. Table B also shows the intensities given by Blix for the reflections from the various hexagonal planes. The intensities agree well with those given by Carlile and Hume-Rothery, and there seems little doubt that, in spite of the different conclusion which they reached, the phase formed in their alloys is the hexagonal phase Cr_2N , in which perhaps manganese replaces chromium to a considerable extent. We cannot share their expectation that manganese will expand the chromium nitride lattice, since Öhman ‡ has stated that in the isomorphous chromium and manganese carbides the spacings are the same in both cases and similar considerations may apply to the nitrides.

† *Loc. cit.*

‡ E. Öhman, *Jernkontorets Ann.*, 1944, 128, 13.

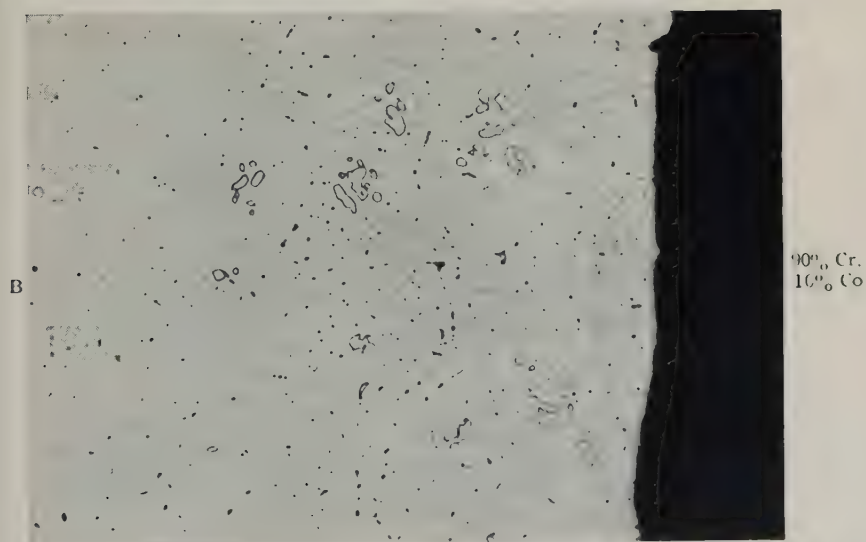
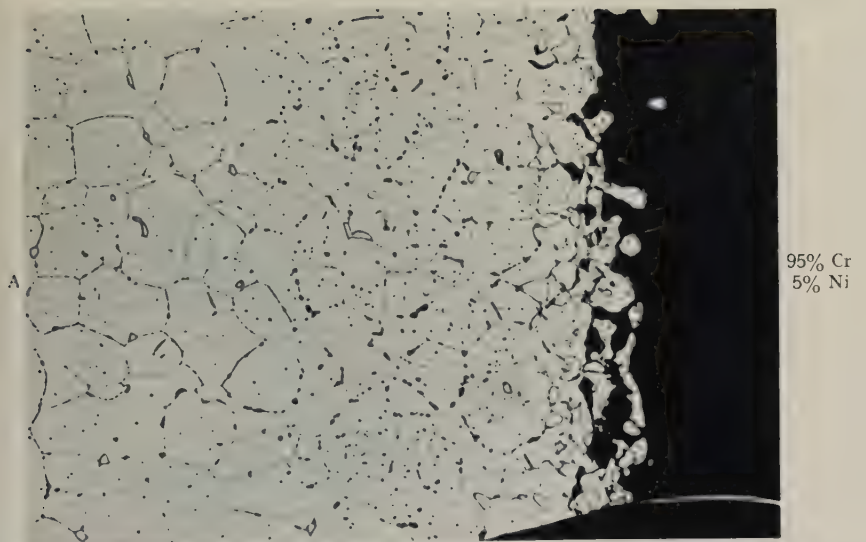
Table C lists Carlile and Hume-Rothery's lines for the hexagonal phase expressed as d values (where $d = \frac{\lambda}{2 \sin \theta}$) and compares these values with the lines, additional to those of the metal, which we obtained from a chromium-30% manganese alloy, a chromium-10% cobalt alloy, and chromium, after melting in air. The films were in all cases taken with unfiltered chromium radiation; d values calculated from the angles given by Blix for the Cr_2N phase are also listed for comparison.

It will be seen that the lines detected correspond to the strongest lines of the pattern from the hexagonal phase in all three cases, the only difference being small increases in the lattice spacings as the alloying addition becomes less. It appears to be clear, therefore, that all these alloys form a nitride isomorphous with the hexagonal Cr_2N phase noted by Blix. We consider that the most interesting feature of Carlile and Hume-Rothery's work is not the nature of this phase but the fact that the susceptibility of the alloys to form nitride at low partial pressures of nitrogen is particularly marked in the range of composition 20-65% manganese.

DR. W. HUME-ROTHERY and MR. W. B. PEARSON (*in reply*): We thank Dr. Sully and Mr. Heal for their interesting communication and for their courtesy in allowing us time to examine the problem further. We regret that a most unfortunate mistake has occurred in this paper and apologize for the confusion which has resulted. Column *B* on p. 197 gave the complete analysis of a portion of an alloy which on prolonged annealing had been converted into the nitride denoted X , and as stated in the paper microscopical examination suggested that the material was homogeneous X , although the presence of cracks made it possible that other constituents might have escaped notice. Examination has now revealed that for some unexplained reason the X-ray powder photograph, the results from which are given in Table I of the paper, is not that of the substance which was analysed, but a photograph of another specimen which microscopical examination indicated as being "homogeneous X " but which was not analysed. Dr. Sully and Mr. Heal are quite correct in saying that the substance whose diffraction lines were described was a mixture of unchanged body-centred cubic alloy with a nitride similar to that investigated by Blix,* and we are unable to say why the lines of the chromium-base solid solution were not recognized. Our re-examination of the problem has fortunately led to a more complete understanding of the structure of the substance, and it is hoped that the following summary may be of interest.

A sample of the product whose analysis was given in column *B* (p. 197) has been submitted to a long exposure with unfiltered Cr radiation in a standard 9 cm. Unicam camera. The resulting film showed 29 lines, but did not include the lines of the body-centred cubic solid solution of manganese in chromium. Fourteen of the stronger lines on the film were identified with a close-packed hexagonal structure of axial ratio $c/a = 1.620$, and $a = 2.759$ kX. This is similar to the structure found by Dr. Sully and Mr. Heal for the lines on the incompletely nitrated powder, but the numerous faint lines indicated that the substance was more complicated. Further examination showed that five of the additional lines, together with the above-mentioned 14 lines, were accounted for by a hexagonal structure with a unit cell whose volume is three times that of the unit of the simple close-packed hexagonal structure. In the larger cell the c axis is the same as that of the smaller cell, whilst the a axis is multiplied by $\sqrt{3}$, so that the axial ratio is $1.620 \div \sqrt{3} = 0.9353$. The relation between the two unit cells is shown in Fig. D which represents one

* *Loc. cit.*



FIGS. A and B.—Nitrogen pick-up and internal oxidation on heat-treatment of chromium-base alloys for 24 hr. at 1250° C., sealed in evacuated silica tubes. Oxide dark; nitride particles light. $\times 100$. (Hardy.)

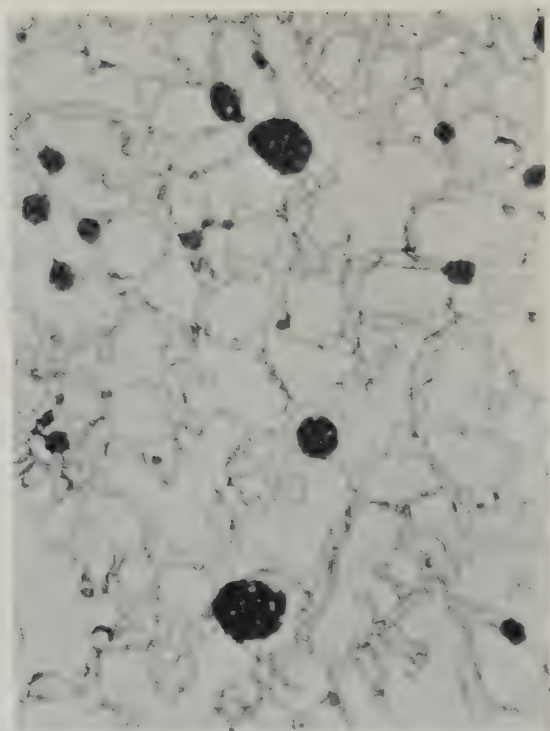


FIG. C.—Structure of chromium after melting in air. Showing oxide (black) and nitrogen-rich phase in chromium matrix. Etched in 50% HCl. $\times 500$. (*Sully and Heal.*)

close-packed layer of atoms. $ABCD$ represents the base of the usual cell of the close-packed hexagonal structure, whilst $EFGH$ is the base of the larger cell which has been rotated through an angle of 30° relative to the normal cell, with a corresponding change in the indices of all reflections except those of the $(00l)$ type. A larger cell of this kind has been described for Cr_2N by Eriksson.* In Table D are shown the lines observed on this film, together with the identification, and it is clear that the main constituent of the powder is based on the hexagonal cell with $c/a = 0.9353$ and $a = 4.779$ kX. It should be noted that some of the observed lines, although fitting the larger cell, would not be expected for the Cr_2N structure of Eriksson. This is presumably because the composition of the powder is more nearly that of $(\text{CrMn})_3\text{N}$ than $(\text{CrMn})_2\text{N}$, and the additional lines might be explained by the ordered removal of nitrogen atoms. It is hoped to investigate later the problem of the distribution of the nitrogen atoms.

The larger hexagonal cell described above did not account for all the lines on the film, but left a number of lines all of which were faint and some fuzzy. Examination then showed that all but two of these could be explained by the ex-

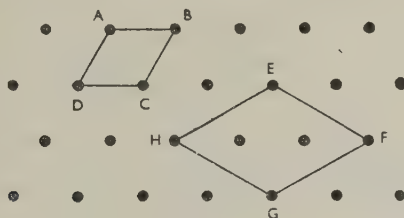


FIG. D.

istence of a cubic structure with $a = \text{approx. } 8.45$ kX. Most of the lines observed were such that h, k, l were either all odd or all even, and in the $(h k o)$ reflections $(h + k)$ was a multiple of 4. This led to the identification of the substance as a spinel, and a literature research showed that Clark, Ally, and Badger † had prepared a synthetic spinel Cr_2MnO_4 with $a = 8.436$ kX., whilst a value of $a = 8.487$ kX. was given by Holgersson.‡ Of the missing spinel reflections, (111) , (222) , (444) , and $(155) + (117)$ are extremely weak; whilst (222) , (400) , (422) , (440) , (533) would overlap the lines at 27.84° , 32.86° , 41.57° , 50.21° , and 62.37° from the hexagonal phase. Examination of Table D shows that all but five of the lines are accounted for by the hexagonal and ideal spinel phases. Of the extra lines, that at 24.07° is very faint and broad and has not been explained. The extremely weak line § at 51.23° might correspond with the $(\Sigma h^2 = 33)$ line of the cubic structure, for which it would give $a = 8.423$; whilst the wide and fuzzy line at the low-angle side of the $(302)\alpha_1$ line of the hexagonal phase covers the position of the $(\Sigma h^2 = 45)$ line of this cubic phase, and the line at 78.107° corresponds with the $(\Sigma h^2 = 52)$ line, giving $a = 8.42$ kX. These three lines would therefore not be those of a spinel arrangement. A pure spinel structure requires the exact composition A_2BO_4 , in

* S. Eriksson, *Jernkontorets Ann.*, 1934, **118**, 530.

† G. L. Clark, A. Ally, and A. E. Badger, *Amer. J. Sci.*, 1931, [v], **22**, 539.

‡ S. Holgersson, *Lunds Univ. Arsskr.*, 1927, **23**, (9); see also P. P. Ewald and C. Herrmann, "Strukturbericht 1913-28", Vol. I, p. 417. Leipzig: 1931 (Akademische Verlagsgesellschaft G.m.b.H.).

§ On measuring the film this line was marked "vvv faint? may be illusory" and we do not think it justifies calculation.

order that each *B* atom shall be at the centre of a tetrahedron of oxygen atoms, and each *A* atom at the alternate corners of a cube whose other corners are

TABLE D.

Bragg Angle of Reflection	Intensity	Hexagonal Phase		Cubic Phase.	
		Index	Value of <i>a</i> (calculated for $c/a = 0.9353$), kX.	Index	Value of <i>a</i> , kX.
22.057°	f	(101) <i>a</i>	4.79
25.585°	vvf	(220) <i>a</i>	8.42
24.07(4)°	vvf and broad	see text	...
25.784°	f	(110) <i>β</i>	4.78
26.654°	mf and broad	(113) <i>a</i>	8.45
27.842°	mf	(002) <i>β</i>	4.76
28.569°	ms	(110) <i>a</i>	4.78
29.589°	ms	(111) <i>β</i>	4.78
30.895°	ms	(002) <i>a</i>	4.76
32.858°	vs	(111) <i>a</i>	4.78
39.662°	f	(112) <i>β</i>	4.77
41.568°	?	(120) <i>β</i>	4.79
44.458°	s	(112) <i>a</i>	4.78
44.831°	vvf?	(333)(511) <i>a</i>	8.43
46.842°	mf	(120) <i>a</i>	4.788
48.983°	f and broad	(300) <i>β</i>	4.776
50.209°	f	(003) <i>a</i> *	4.772
		(121) <i>a</i> *	4.815
51.23°	vvf?	see text	...
	Broad and fuzzy on low-angle side of next line	(531) <i>a</i>	8.45
55.940°	s	(300) <i>a</i>	4.780
58.770°	f	(620) <i>a</i>	8.455
62.369°	f	(302) <i>β</i>	4.780
63.211°	f	(122) <i>a</i>	4.775
64.698°	s	(113) <i>a</i>	4.780
65.549°	f	see text	...
	Broad and fuzzy on low-angle side of next line	see text	...
76.683°	s	(302) <i>a</i> ₁	4.780
78.107°	f	see text	...
81.802°	ms?	(221) <i>a</i> ₁	4.779
		<i>a</i> ₂	not clear		

vs = very strong, s = strong, ms = medium strong, f = faint, vf = very faint, vvf = extremely faint. Where a line is marked vvf? it means that the line was too faint for any accurate measurement.

* These two lines are very close together.

occupied by oxygen atoms. It seems reasonable, accordingly, to suggest that the faint and fuzzy lines originate from a substance whose structure is essentially of the spinel type, and that the extra lines which fit the same cubic lattice are due to a composition differing slightly from the ideal Cr_2MnO_4 . The results suggest strongly that when the atomic ratio of manganese to

chromium is approximately 1 : 2, the action of oxygen at very low pressures is to produce a substance of the spinel type.*

To examine the matter further the small remaining amount of powder was treated with 2*N*-sulphuric acid in order to dissolve the nitride, and a further diffraction film taken of the residue. This now gave lines corresponding to the spinel structure, but the lattice spacing had fallen to $a = 8.418$ kX.† The film also contained faint lines due to α -SiO₂, and these unfortunately prevented a conclusive decision as to the nature of the lines corresponding to $\Sigma h^2 = 33$ and 45 of cubic structure. The amount of material was too small to permit further examination or chemical analysis.

The suggestion of Dr. Sully and Mr. Heal that manganese will not expand the chromium nitride lattice is contrary to known facts. The lattice constants for Cr₂N change from $a = 2.747$, $c = 4.439$ kX. to $a = 2.770$, $c = 4.474$ kX. on passing from the chromium-rich to the nitrogen-rich boundary,‡ while the lattice constants for the isomorphous Mn₂N phase change from $a = 2.773$, $c = 4.520$ kX. at 9.2 wt.-% nitrogen to $a = 2.828$, $c = 4.528$ kX. at 12.1% nitrogen, the homogeneous region lying probably between 9.2 and 11.9% nitrogen at 400° C.§ The manganese nitride lattice is therefore larger than the chromium nitride lattice. The lattice constants reported for the chromium-manganese nitride, $a = 2.759$, $c = 4.470$ kX., are, as the analytical figures show, reasonably comparable with the values given above for the nitrogen-poor boundaries of the chromium and manganese hexagonal nitrides. It is therefore apparent that manganese expands the chromium nitride lattice.

* It may be noted that electron-diffraction methods have detected the presence of spinels in the surface layers of oxidized alloys of transition metals (E. A. Gulbransen, R. T. Phelps, and J. W. Hickman, *Indust. and Eng. Chem. (Analyt. Edn.)*, 1946, **18**, 640).

† The following lines were identified: (111) α , (220) α and β , (113) α and β , (400) α and β , (422) α , (333) α and β , (440) α and β , (260) α , (335) α and β , and (444) α .

‡ R. Blix, *loc. cit.*

§ G. Hägg, *Z. physikal. Chem.*, 1929, [B], **4**, 346.

DISCUSSION ON THE PAPER BY MR. J. CROWTHER : " OVERHEATING PHENOMENA IN ALUMINIUM-COPPER-MAGNESIUM-SILICON ALLOYS OF THE DURALUMIN TYPE."

(*J. Inst. Metals*, this vol., p. 201.)

PROFESSOR L. F. MONDOLFO,* Dr. Eng. (Member) : One point that I think has not been emphasized is the appearance of the eutectic melting, and its effect on the properties. Eutectic melting can occur in two different forms, as melting at the grain boundaries, which leads to cracking and extensive deterioration of the properties, or in the form of small globules (rosettes) of eutectic inside the grains, whose effect on properties is very limited. Figs. 22 and 24 (Plate XXIV) of the paper show typical examples. The first type is more liable to occur in castings or insufficiently deformed wrought products; the second in well-homogenized materials such as thin sheet or wire. In my experience this last type of melting can appear alone and not affect the properties sufficiently to be noticeable.

I think that the influence of iron and manganese should also be investigated, not because they affect the melting points of the eutectics, as pointed out by the author, but because they will affect appreciably the amount of silicon and copper available for the formation of eutectics. In this respect, I have noticed that with magnesium : silicon ratios of more than 1.73 (Mg_2Si) there is a tendency for the $AlCuFeMn$ compound to form, whereas with higher silicon content the $AlMnFeSi$ compound tends to appear.

PROFESSOR CYRIL STANLEY SMITH † Sc.D. (Honorary Corresponding Member to the Council for the U.S.A.) : I have discussed elsewhere ‡ the importance of interface energy in determining the microstructure of alloys, and showed how the ratio between the energy of a grain boundary and that of the interface between the two phases determines whether the second phase, either solid or liquid, spreads between the grains or exists in a more or less compact form. Such intergranular spreading, of course, is at the very root of the question of overheating.

Measurements of interface equilibrium angles have been made on a number of aluminium alloys containing liquid,§ and it was found that in not all cases does the liquid spread completely between the grains. The authors seem to assume (pp. 203-204) that the presence of a liquid phase in an alloy invariably gives grain-boundary films and is inevitably bad. This is a common assumption among metallurgists, who will often say that the onset of brittleness on heating is a sensitive method of determining the solidus temperature of an alloy. Actually, extreme brittleness occurs only if the "dihedral angle" of the liquid phase is zero or nearly zero, which means that the ratio of inter-

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‡ C. S. Smith, *Trans. Amer. Inst. Min. Met. Eng.*, 1948, 175, 15.

§ K. K. Ikeuye and C. S. Smith, *Trans. Amer. Inst. Min. Met. Eng.* (in *J. Metals*), 1949, 185, 762.

face energies must not greatly exceed 0.5. This criterion simply means that the two interfaces between liquid and solid together have less energy than does the single grain boundary that they replace. If this is not so, normal grain boundaries will occupy at least part of the total interface area and the liquid will be partially restricted to grain corners. If the ratio is between 0.5 and 0.577 (i.e. if the dihedral angle is between 0° and 60°), the liquid phase will still be continuous along grain edges throughout the entire piece, but it will not entirely separate the grain faces. As the ratio progressively exceeds 0.577 the second phase will tend more and more to a spherical shape and it will be continuous only when present in excess. If the angle is less than 60° , then the second phase forms a continuous network, however little of it there may be (in excess of a monomolecular film), unless the liquid is trapped in the body of the grain out of contact with any grain boundary.

The effective angle is clearly demonstrated in the difference between the author's Fig. 25 and Fig. 26 (Plate XXIV). The grain-corner melting in Fig. 25 appears to correspond to a dihedral angle of about 30° . Fig. 26 clearly corresponds to a zero dihedral angle, for there is complete separation of the grains by a film of liquid. The spherical drops of liquid that are shown in the author's Fig. 24 occur, as he points out, only in the centre of grains. In the absence of a grain boundary there is only one interface to be considered and this inevitably takes the shape approximating a sphere.

The interface energy ratio, Γ , is characteristic of a given composition of the two phases in contact with each other, and is relatively unaffected by temperature, except insofar as temperature affects the composition. The latter is frequently very important. In aluminium-tin alloys,* for example, at temperatures just above the eutectic temperature the dihedral angle is 55° and, though the liquid is continuous, it forms a prismatic network only along grain edges. It does not penetrate between the grains and therefore is not extremely harmful to the ductility of the alloy. As the temperature is raised, the aluminium content of the liquid increases and with this the energy of the interface between aluminium crystals and the liquid alloy decreases. As this happens, the dihedral angle becomes smaller and the liquid in attaining surface-tension equilibrium (or rather minimum total surface energy) penetrates further and further between the grains. As it does so the mechanical properties become more and more adversely affected.

The results of measurements of this angle in aluminium-tin alloys are shown in Fig. A. An alloy with 10% tin was cold worked, then annealed at temperatures between 250° and 650° C., and rapidly quenched. After metallographic preparation, the angles of the corners of the tin droplets where they met the aluminium grain boundaries were measured and the statistically most frequent angle found. The interface energy ratio is then :

$$\Gamma = \frac{\gamma_{al}}{\gamma_{aa}} = \frac{1}{2 \cos \frac{\theta}{2}}$$

where γ_{al} is the energy (free energy) of the interface between a crystal and liquid, γ_{aa} is the energy of the grain boundary between two α grains, and θ is the dihedral angle of the liquid, measured under the microscope after quenching. The composition of the liquid used in plotting Fig. A is taken from the new liquidus determined by Sully *et al.*† The variation of Γ with composition is strongly reminiscent of the variation with composition of the surface energy of a liquid binary alloy.

If, as a result of a peritectic or monotectic transformation, the composition

* K. K. Ikeuye and C. S. Smith, *loc. cit.*

† A. H. Sully, H. K. Hardy, and T. J. Heal, *J. Inst. Metals*, 1949-50, **76**, 269.

of the liquid phase in an alloy should discontinuously change at a certain temperature, one would expect the interface energies to change suddenly and with it the extent of damage due to overheating.

It is perhaps surprising that such rudimentary surface-energy concepts are applicable to so many solid or partly solid structures. One might have anticipated that interface energies would be strongly dependent on crystallographic orientation, yet the gently curved shape of grain boundaries and the essentially spherical nature of liquid inclusions within grains shows that such effects are minor. Only when grains differ but little in orientation, either from an exact match or from twin positions, is the energy greatly orientation-sensitive, and grain boundaries of this character are statistically rather unimportant.*

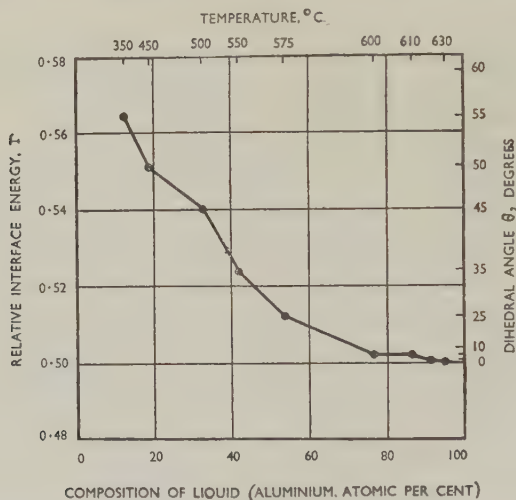


FIG. A.—Variation with Temperature and Composition of Liquid Phase of Interface Energy Ratio in Aluminium-Tin Alloys.

I believe that those concerned with overheating phenomena or with other aspects of the influence of liquid phases in alloys, will find it useful to measure the dihedral angles and to plan variations of composition and treatment in accordance with the general concepts of surface energy.

The AUTHOR (*in reply*): Replying to Professor Mondolfo, I agree that the two types of liquation, by grain-boundary films and by globules within the grains, have quite different effects on quench-cracking and on mechanical properties in the cold; this difference is mentioned on p. 205 of the paper. In my opinion, the formation of globules demonstrates the microscale variation in chemical composition in the solid-solution matrix, which gives rise to preferred centres of liquefaction within the grains in addition to those along the grain boundaries. When alloys of the type discussed have been fairly extensively worked and recrystallized, the existing grain pattern bears no relationship to the original cast grain pattern, so that the dendritic coring which persists, however faintly, will give an apparently random distribution of such

* W. Shockley and W. T. Read, *Phys. Rev.*, 1949, [ii], 75, 692.

centres. Globules should, therefore, be most obvious in moderately worked material not fully homogenized. Since local melting involves a diffusion of alloying elements into the liquid from the surrounding solid, large-grained material also will tend to show a higher proportion of liquid within the grains, the diffusion to centres within the grains taking place over shorter distances than diffusion to the grain boundaries (p. 204). No systematic work was done on the effect of manganese and iron, since this appeared to be a secondary factor.

Professor C. S. Smith's contribution is particularly welcome. Most of the work on overheating was completed when his classic paper appeared in 1948, but the relevance of his ideas was obvious. The results of micro-examination of liquated sheet specimens are given on p. 234 of the present paper, suggesting that liquation at the $\text{Al} + \text{CuAl}_2 + \text{Mg}_2\text{Si} + Q$ plane was somewhat different from that at other points on the solidus. A little further work was done but was not sufficiently conclusive to be included in the paper. A melt was made of the approximate composition of each eutectic of the system and a rod of composition roughly that of the solid solution in equilibrium with it was dipped into the melt through a layer of flux. On withdrawal the rod carried a layer of eutectic and was held for some time at a temperature 2°C . higher than the melting point of the eutectic before being allowed to solidify slowly. Microsections then showed a resolvable eutectic structure where penetration had taken place. Very active penetration was observed with the $\text{Al} + \text{CuAl}_2 + \text{Mg}_2\text{Si}$, $\text{Al} + \text{CuAl}_2 + Q + \text{Si}$, and $\text{Al} + \text{CuAl}_2 + S$ eutectics, the boundaries being completely wetted over a distance of $\frac{1}{2}$ in. by films never more than 3×10^{-4} in. thick, except at grain corners. The $\text{Al} + \text{CuAl}_2 + S$ eutectic gave films very much thinner than this. No positive evidence of penetration was obtained with other eutectics tried, but this was probably due to incorrect composition of the solid-solution alloy. No penetration at grain edges only was observed with any eutectic.

This series of tests did not cover the 514°C . part of the solidus, since the composition of the melt required was not known.

DISCUSSION ON THE PAPER BY DR. W. A. WOOD AND MR. W. A. RACHINGER: "THE MECHANISM OF DEFORMATION IN METALS, WITH SPECIAL REFERENCE TO CREEP."

(*J. Inst. Metals*, this vol., p. 237.)

The AUTHORS*: We find that our conclusions often show an interesting parallel with the partly forgotten concepts of amorphous and viscous layers advanced by the older metallurgists, especially by Rosenhain, which appear as a curiously far-sighted appraisal of the evidence then available.

In this type of work on deformation it is known that the grains of a polycrystalline aggregate tend to follow the external shape of the test specimen. Relative grain movements and random boundary migrations may be superposed, especially at the higher temperatures of deformation, but the essential feature to be explained is the imposed change in shape of the individual grain, and this is the underlying aim of the work.

(1) We suggest first that, in general, the change in shape necessitates a dissociation of the grain into conveniently-sized elements that develop sufficient difference in relative orientations to give them some separate entity. We show that this size then depends systematically on the temperature and rate of strain. This dependence has led us to the recognition of three basic mechanisms of deformation:

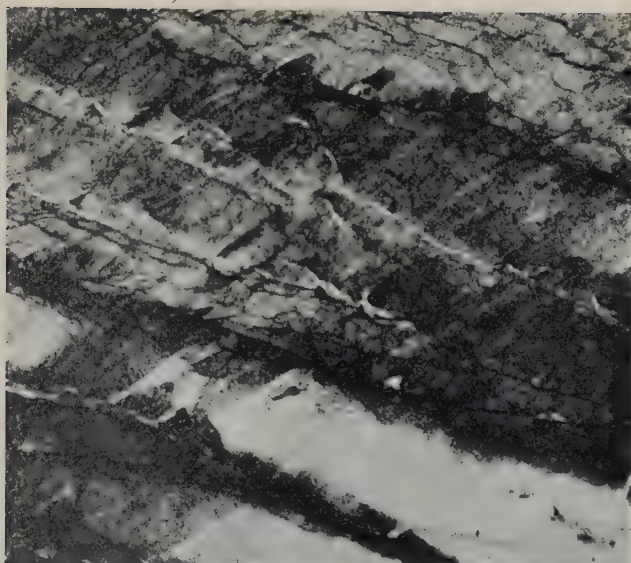
(i) *Slip Mechanism*.—This becomes a mechanism associated with the most drastic dissociation, predominating at the lower temperatures or higher rates of strain. The resulting sub-structure is pictured as consisting of blocks that correspond broadly with the regions between the slip lines, together with material in a finer state of sub-division in the slip zones between the blocks. This material, or debris as it were, we have referred to in other work as crystallites. We believe we can show that the zones between the blocks do in fact consist in the main of such debris rather than zones of lattice distortions or curvatures. The main point, however, is the finer sub-division of the grain when slip occurs.

(ii) *Cell Mechanism*.—This mechanism is then one associated with a less drastic dissociation and one that supersedes the above as the temperature of deformation is increased or rate of strain decreased. The characteristics of the sub-structure are the greater size of the blocks, the virtual absence of crystallite debris or related distortion, and the absence of slip lines. It is a significant point that when there is no utilization of slip planes there is no detectable crystallite debris or related distortion.

(iii) *Boundary-Flow Mechanism*.—We are next led to this mechanism as an interesting logical consequence of the last one. Our results show that in the cell mechanism, the size of the elements increases systematically with increasing temperature of deformation and decreasing strain rate. It follows that finally a stage will be reached when the size of the cells will approach that of the grain itself; and actually in later work we have produced this condition. At this stage then the grain cannot change shape by sub-division as before. Therefore it can do so only by some kind of atomic flow in the boundary zone.

* Remarks made in introducing the paper for discussion at the Annual General Meeting of the Institute held in London, March 1950.

direction of slip traces



direction of deformation-band traces

FIG. B.—X-ray Micrograph of an Aluminium Crystal after 2 days' straining at 300° C. $\times 20$. (*Honeycombe and Brown.*)



FIG. C.—X-ray Micrograph of Same Area as Fig. B after 4 days' straining at 300° C. $\times 20$. (*Honeycombe and Brown.*)

[To face p. 730.]

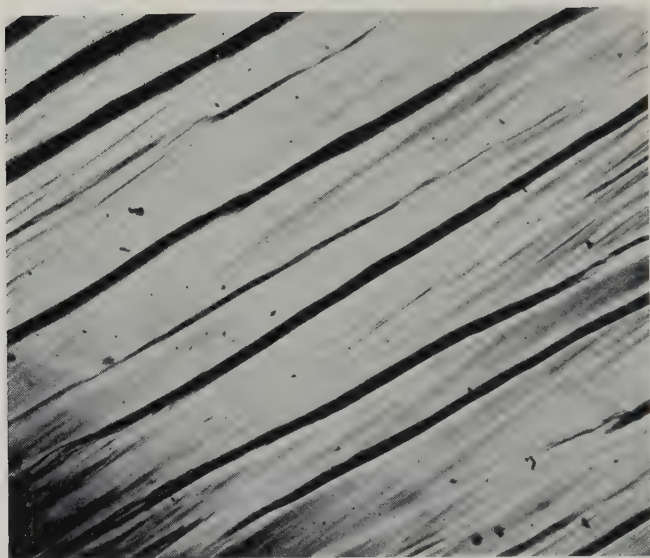


FIG. D.—Optical Photomicrograph Corresponding to Fig. B (Plate CX).
× 50. (*Honeycombe and Brown.*)

By a process of elimination we thus reach this third mechanism of a "boundary flow" and show its place in the general scheme.

(2) We feel that the explanation of these three stages of deformation will be found in the condition of the grain boundaries. It would appear that at sufficiently elevated temperatures and low rates of deformation the boundary atoms themselves have enough mobility *and time* to produce the required change in shape of the grain, so that there is no need for a sub-structure; then the third mechanism predominates. But at the other extreme, of low temperature and high strain rate, the boundary zone is frozen into inactivity and a drastic breakdown is necessitated; this occurs most efficiently by utilization of the slip planes, giving rise to the sub-structure associated with the slip mechanism. Finally, at intermediate temperatures and strain rates, the boundary may be expected to become partially active, resulting in the less drastic sub-structure of the cell mechanism.

There is an obvious similarity to the old idea of "equi-cohesive" temperature. But we should not recognize an absolute temperature. We show that the factor of strain-rate is equally important. So also is the *amount* of available grain-boundary material, that is, the grain-size of the specimen, in determining which mechanism will predominate.

(3) We should like to emphasize that there is a wide difference between the production of sub-structures by simultaneous deformation and heating as in creep, and their production when deformation and heat-treatment are applied separately as in experiments on "recovery" from cold-work. In recovery, as usually understood, a specimen is deformed cold and by the slip mechanism. It is a lower limiting case of the production of sub-structures at higher temperatures and slower strain-rates and, as shown in the paper, the cold-worked structure is therefore associated with a very fine sub-structure and accompanied by crystallite debris or distortion. There is no reason why heating this sub-structure should reproduce those formed by the action of deformation at a higher temperature. Indeed we have been able to show that all the heating does is to clarify the fine sub-structure, but not to produce any noteworthy growth. This clarification or "recovery" would be explained by some workers as due to the process termed polygonization. We prefer the simpler explanation that the recovery is due to the partial absorption of the crystallite debris into the larger blocks originally formed by the slip mechanism.

(4) In conclusion, a further point perhaps worthy of attention is the observation of the equilibrium in respect of size and orientation of the sub-structures that sets in for a given strain-rate and temperature. We find that this equilibrium structure is the same whether produced in the secondary stage of creep as in ordinary creep testing, or whether the same strain-rate is imposed forcibly as in the present work. Moreover, it continues throughout the secondary-creep stage and until the final acceleration that precipitates fracture.

Through the observation of this equilibrium we can offer an explanation of creep on the hypothesis that the strength of the metallic grain is determined by the size of the constituent crystalline elements. For it follows that when the equilibrium is established, strain-hardening will then cease. This possibly is one of the more important contributions of this work to the theory of creep.

DR. N. P. ALLEN,* M.Met., F.I.M. (Member) : Dr. Wood and Mr. Rachinger have performed a useful service in showing that the processes of plastic deformation undergo systematic alterations with temperature, and that the processes involved in slow deformation at a low temperature are in many ways similar to those involved in rapid deformation at a somewhat higher tem-

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perature; but they probably overstrain their evidence in drawing too sharp a distinction between the "cell" and "slip" mechanisms of deformation. They state for example that slip lines were absent in specimens that had been strained slowly above 250° C. and offer in support photomicrographs taken at $\times 100$. But in specimens of this kind many very fine slip lines are present, and even in samples that under ordinary illumination appear free from them at $\times 500$, slip lines may be revealed by more sensitive methods of illumination, such as the phase-contrast method. The "cells" are estimated to be from 1 to 7×10^{-4} cm. across, and to have differences of orientation of about 0.1–0.2°. They should thus produce differences in level in the polished surface of some 50–250 Å. These should be readily visible in the phase-contrast microscope, and it ought to be possible to observe and measure them. Incidentally, the cells seen in Fig. 2 of the earlier paper by Wilms and Wood* seem unlikely to be the same as the "elements" whose size has now been measured by X-ray methods, if the X-ray measurements are correct, since they are several times larger than would be expected. The conclusion that the size of the sub-structure is directly related to the stress applied to the metal during deformation would be an extremely important one if it could be relied upon, but it will be felt that the amount of evidence offered, though sufficient to permit the idea to be entertained, is scarcely sufficient to prove the point. The authors have not tabled a list of measured dimensions of the sub-structure along with the corresponding resistances to deformation and judgment could well be reserved until this has been done.

DR. M. L. V. GAYLER (Member): The authors have found that, under slow straining, deformation proceeds at each temperature by a similar relative movement of discrete elements into which the grain has dissociated, but that as the elements composing the sub-structure become less than a critical size, there is a transition from the "cell" mechanism to the mechanism of deformation by slip. They also remark: "This change . . . is of special interest when it is realized that the corresponding X-ray photographs show only a progressive refinement of the sub-structure as the temperature of deformation is reduced from 350° C." I think, however, that if the authors would repolish (electrolytically) the strained surfaces showing slip deformation, and then etch them, further information on this phenomenon would be obtained. It may not be easy to etch the surfaces so that a structure is revealed, but an effective reagent can probably be found.

I would suggest that, when deformation by slip sets in at temperatures up to 150°–200° C., the fine-sized structure observed by X-rays is the result of the relief of strain in highly localized areas in the region of slip, and that "crystallites" are formed such as I found † along the lines of slip during the microscopical examination of a cold-worked and aged high-purity aluminium-4% copper alloy (see Figs. 18, 20, 29, 30, and 31 of my paper). Wood ‡ had previously discovered by X-ray analysis that on the progressive cold working of aluminium the grains are dispersed into fundamental units (crystallites), characterized by a lower limiting size. The size found for aluminium, i.e. about 10^{-4} cm., was of the same order as that of the "crystallites" which I had observed. I therefore concluded § that the two were probably identical, and I now suggest that they also form the sub-structure observed by Wood and Rachinger at temperatures below and up to about 200° C. during creep.

* G. R. Wilms and W. A. Wood, *J. Inst. Metals*, 1948–49, 75, 693.

† M. L. V. Gayler, *J. Inst. Metals*, 1946, 72, 543.

‡ W. A. Wood, *Proc. Roy. Soc.*, 1939, [A], 172, 231.

§ M. L. V. Gayler, *J. Inst. Metals*, 1947, 73, 681.

In my opinion, their appearance indicates that relief of highly localized stress is taking place during creep by the process of local recrystallization of the lattice in those regions, i.e. crystallite formation. As suggested above, it should be possible to prove or disprove this by further microscopical analysis.

At temperatures above 200° C. the authors have found that deformation by "cell" formation takes place. In this case, also, I suggest that relief of stress is occurring but by a different recrystallization process, i.e. by polygonization, such as Cahn * has described. Microscopical examination, carried out on repolished and etched specimens, previously strained at temperatures of 250°-350° C., might also throw further light on the nature of the "cell" mechanism of deformation.

Mr. A. GRAHAM,† M.Sc.: The authors have clearly demonstrated a qualitative equivalence of the effects of straining-rate and temperature on the mode of deformation, and it is interesting to see that their results are in quantitative agreement with a relationship that has been established in terms of mechanical behaviour.

MacGregor and Fisher ‡ have shown, for a number of materials and a wide range of conditions, that stress is a function of strain and a quantity :

$$T_m = T \left(1 - k \log \frac{\dot{\epsilon}}{\dot{\epsilon}_0} \right),$$

in which $\dot{\epsilon}$ is the rate of straining, T the absolute temperature, and k and $\dot{\epsilon}_0$ are constants. Their value of k for aluminium (for $\dot{\epsilon}_0 = 10^{-7}$ /sec. and log to base 10) is 0.077. For other materials values ranging between 0.02 and 0.10 are found. According to this view, the stress/strain relation is unaffected by a change of temperature provided the straining-rate is so changed simultaneously as to maintain the value of T_m .

TABLE A.

Fast Deformation $\dot{\epsilon} = 1.7 \times 10^{-3}$ /sec.		Slow Deformation $\dot{\epsilon} = 2.8 \times 10^{-7}$ /sec.	k
X-Ray Patterns	200° C.	corresponds to 20° C.	0.096
	250	150	0.049
	350	110	0.094
	400	200-250	0.067
	500	250-300	0.074
			Mean 0.076
Photomicrographs	200-250° C.	110-150° C.	0.049
	350	200-150	0.072
	400	200	0.076
	500	300	0.066
			Mean 0.066
			Overall Mean 0.071

Wood and Rachinger's pictures can be arranged in pairs, one for fast and one for slow deformation, which have substantially the same diffraction pattern or the same appearance in the microscope. These pairs and corresponding values of k are shown in Table A.

The two sets agree and the final mean is in good agreement with MacGregor

* R. W. Cahn, *J. Inst. Metals*, 1949-50, **76**, 121.

† National Gas Turbine Establishment, Whetstone, Leicester.

‡ C. W. MacGregor and J. W. Fisher, *J. Appl. Mechanics*, 1945, **12**, A217; 1946, **13**, A11.

and Fisher's value. Unfortunately the author's own mechanical-test data are insufficient for analysis.

It is interesting to notice that MacGregor and Fisher investigated plain carbon steels from -70° to $+665^{\circ}$ C., i.e. probably from extremes of low- to high-temperature modes of deformation, and found no need to change k in this range. This quantity may not therefore alter with the mode of deformation.

MR. R. W. K. HONEYCOMBE,* M.Sc. (Member), and DR. A. F. BROWN:† There seems no doubt that the phenomenon of fragmentation occurring in creep specimens of aluminium at elevated temperatures is identical with the polygonization described in Cahn's ‡ paper. We think, however, that it is a matter for some discussion whether the high-temperature fragmentation can be extrapolated to room temperature as the authors have done; furthermore, the possibility of deformation by slip should not be excluded because the slip zones cannot be detected in the microscope.

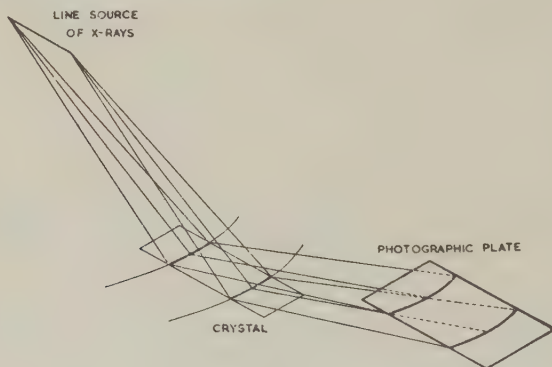


FIG. A.

We would like to mention briefly some work which we have been doing which may help to decide the points raised. We have been studying the creep of aluminium both at room temperatures and at elevated temperatures in single crystals and coarsely crystalline aggregates, and have used two experimental approaches. Firstly, conventional optical micrograph and electron micrograph, and secondly, a technique of X-ray micrograph similar to that described by Berg ‡ and more recently by Barrett.§ The principle of this technique is shown in Fig. A. An X-ray beam from a line focus falls on a crystal which is rotated until a Bragg reflection occurs. The reflection represents a point-for-point image of the crystal surface, and changes in orientation such as local rotations or bendings are revealed as striations in the image.|| The resolution is quite high and the resulting images on magnification to 50 dia. reveal fine detail. In our experiments we have electropolished large single crystals of aluminium and then subjected them to slow straining at creep rate (usually about 0.8% elongation/day). After several days' straining the crystals are examined optically and by the X-ray technique. The first point

* Cavendish Laboratory, Cambridge.

† R. W. Cahn, *J. Inst. Metals*, 1949-50, **76**, 121.

‡ W. Berg, *Z. Krist.*, 1934, **89**, 286.

§ C. S. Barrett, *Trans. Amer. Inst. Min. Met. Eng.*, 1945, **161**, 15.

|| R. W. K. Honeycombe, *Proc. Phys. Soc.*, 1950, [A], **63**, 673.

is that, optically, slip zones are always observed even after deformation at temperatures as high as $450^{\circ}\text{C}.$; however, at this temperature the slip zones are extremely coarse and visible to the naked eye. The X-ray technique does not primarily show up these slip lines, but a system of black and white bands. We can now say for certain that these bands are caused by fine deformation bands in the crystal, i.e. narrow regions in which the crystal lattice is sharply bent. They are not only characteristic of deformation by creep but occur in single crystals regardless of the rate of deformation or of the temperature at which it is carried out.

If the slow deformation is prolonged at elevated temperatures (300° – $450^{\circ}\text{C}.$) the pattern of bands is replaced by a pattern which leaves no doubt that the crystal has fragmented into small particles of closely related orientation. There seems to be a very definite relation between the occurrence of the deformation bands and the observed fragmentation of the crystals. This relation is perhaps best shown in experiments carried out on very coarsely crystalline specimens of aluminium which were treated in the same manner as the single crystals. Individual grains were chosen for examination by X-rays and the microscope. It was found that after 0.9% straining in tension in one day at $300^{\circ}\text{C}.$, several of the large grains had developed very coarse slip lines; on the other hand, while the X-ray micrograph taken did show the slip lines clearly, its most striking feature was the development of pronounced deformation bands. After two days (1.8% extension) the bands had become much more pronounced (Fig. B, Plate CX), and fragmentation of the crystal had begun, particularly in the regions of the deformation bands, now seen to be quite complex. It is suggested that these bands, which are regions of lattice curvature, become the boundaries between the fragments of the crystal by polygonization as described by Cahn; by this process the curvature is removed and replaced by a sharp boundary. The length of the polygonized fragment is probably determined by the slip lines which cross the deformation bands. As deformation is proceeding simultaneously with the formation of polygons, it is easy to see that the original long lattice blocks between the deformation bands will be broken up into smaller blocks by the passage of slip zones. We think this is shown clearly in Figs. B and C (Plate CX) which are X-ray photographs taken after two and four days' creep, respectively. For comparison Fig. D (Plate CXI) shows an optical picture of the same region with the very coarse slip zones clearly visible. Deformation bands are not visible in this figure but can be shown up by oblique illumination. Electron-microscope examination of the very coarse slip zones formed in slow straining at high temperatures shows that they are composed of the same lamellæ as those described by Heidenreich and Shockley* and by Brown,† the only difference being that each coarse slip zone may be composed of several dozen lamellæ instead of the half-dozen or so observed with fast straining. The zones are correspondingly further apart—further apart indeed than the dimensions of the grains used by Wood and Rachinger.

There is not space to discuss in detail the mode of formation of the deformation bands, but it does involve some deformation by slip. In our experiments with single crystals and coarse-grained polycrystals, the slip was obvious. In Wood and Rachinger's specimens, which had much finer grain-size, the slip is not seen easily, but is it really absent (see, for example, Fig. 4 in their paper)? If it is, then it is difficult to imagine a mechanism whereby the observed fragmentation occurs.

* R. D. Heidenreich and W. Shockley, *Phys. Soc.: Rep. Conf. on Strength of Solids*, 1948, p. 57.

† A. F. Brown, *Inst. Metals.: Symposium on Metallurgical Applications of the Electron Microscope*, 1949, p. 103. (Monograph and Report Series No. 8.)

The extrapolation of the fragmentation taking place at elevated temperatures to room temperature or lower implies that polygonization occurs at room temperature. This is not so for aluminium single crystals, for while the deformation bands are formed during deformation at room temperature, there is no indication that the bent regions of the lattice change to a polygonized structure (where the crystal lattice becomes discontinuous) at this temperature, even if the deformation is carried out very slowly. Fragmentation of bent regions of the crystal lattice at high temperatures is essentially a recovery mechanism, and it is difficult to see why fragmentation of the *same type* occurs at room temperature or, say, the temperature of liquid air where recovery is not possible.

DR. A. LATIN,* M.Eng. (Member): I think it is an acceptable view, and one which I have myself maintained for some time, that the cellular sub-structure observed by the authors is caused by mechanisms similar to that proposed to explain polygonization. It seems to me that the action taking place in quasi-viscous creep can be explained on the view that there are at least two distinct types of dislocation movement occurring:

(1) The ordinary movement along the glide planes in the direction of the so-called Burgers's vector, that is, the vector which represents the atomic displacement concerned. This is the type of motion of dislocations which is connected with the ordinary process of plastic deformation by slip, but I would suggest the modification that slower speeds are possible.

(2) A motion of dislocations which can be regarded as amounting to a jump from one glide plane to another. This motion, insofar as creep is concerned, can, it seems to me, be regarded as a thermally-activated diffusion process, and will obviously be favoured by increase of temperature. I think it also evident that the proportion of total deformation due to this latter type of dislocation movement will increase with decrease in rate of deformation.

The cellular structures observed by Wood and Rachinger seem to me to be due to the resultant effect of these two dislocation movements, but it is evident that a more detailed consideration of the mechanisms is required to co-ordinate the types of dislocation movement concerned, &c., with the size of the cells, rates of deformation, and temperature.

The AUTHORS (*in reply*): In reply to Dr. Allen, it will be obvious that no metal is likely to deform perfectly uniformly. It would be too much to expect that in one range of temperature and strain-rate the metal should deform by the cell mechanism only and be absolutely free from slip; and in another by pure slip only. What we are pointing out is an obvious gradation from one extreme where the cell mechanism predominates to another extreme where the slip mechanism predominates. The surprising feature rather is that in aluminium, the gradation should be so well-defined as in fact it is. In his further point, Dr. Allen presumably makes a slip when he supposes that a change in internal crystallographic orientation necessitates an equivalent external bodily rotation of a cell.

We have electrolytically repolished various strained specimens, as suggested by Dr. Gayler, but find no evidence that the cells are formed by nucleation at high stress points along slip or deformation bands. All our evidence goes to show they are formed simply by direct breakdown of the grain under the action of deformation. Dr. Gayler's specimen was deformed at room temperature. In such a case the fragmentation is most drastic, and naturally is likely to be most pronounced in those regions where deformation is heaviest. Thus we should expect from our present observations and

* Research Department, British Insulated Callender's Cables, Ltd., London.

the earlier observations by Wood, referred to by Dr. Gayler, that there would be fine crystallites in the vicinity of slip bands, as Dr. Gayler observed. But we think it is quite unnecessary to assume they are due to local "recrystallization".

Mr. Graham provides an interesting confirmation of the general interdependence of temperature and strain-rate. Our results indicate the physical reasons why such a relation should exist in terms of changes in the microstructure of the metal. But such changes at the present stage could hardly be used for quantitative relations except in a very general way.

We have been intrigued by the almost indecent haste with which various commentators on our observations have rushed in with a theory before the phenomena in question have been fully investigated even by ourselves. The remarks by Mr. Honeycombe and Dr. Brown are an example. They begin with the naïve and sweeping generalization that there seems no doubt that the phenomena are identical with polygonization. Their arguments would be more convincing, however, if they could first prove that there is such a process as polygonization. The only theoretical evidence we have seen is dubious in the extreme. The experimental evidence appears to be mainly based on a break-up of asterism streaks in low-resolution X-ray photographs. This break-up can be explained much more naturally by the fact that *deformation* breaks down the grain, and *heating* merely causes partial re-absorption or growth of the smaller rotated fragments that cause the initial diffusion of the asterism streaks. In recent experiments, using higher-resolution X-ray photographs, we have found it possible to observe such growth directly. Moreover, the particular photographs reproduced by Mr. Honeycombe and Dr. Brown can also be explained more simply in the same way without the somewhat unnatural assumption of polygonization that heat-treatment produces disruption of grains! Therefore, far from being convinced that the cells are due to the hypothetical disruptive process of polygonization, we submit that all the evidence available so far suggests that it is due in fact to a reverse process, which we are terming "cell growth".

The above comment applies also to the suggestions made by Dr. Latin. As we interpret the facts, deformation of the grains causes breakdown; heating during deformation causes growth; the sub-structure we observe is the resultant. If there is slip, as there usually is in very coarse grains or single crystals, for the reason pointed out in our introduction to the discussion, the breakdown factor is more drastic, especially in the vicinity of slip or deformation bands. The same factor preponderates with the higher rates of strain.

DISCUSSION ON THE PAPER BY DR. O. KUBASCHIEWSKI AND DR. O. VON GOLDBECK: "ON THE MECHANISM OF OXIDATION OF NICKEL-PLATINUM ALLOYS."

(*J. Inst. Metals*, this vol., p. 255.)

DR. DONALD E. THOMAS*: The study of the oxidation of alloys containing a base metal and a noble metal has long been attractive for the reasons cited by the authors, and has included the systems copper-gold,† § ¶ copper-silver,‡ § copper-palladium,§ gold-silver-copper,§ gold-palladium-copper,§ silver-palladium-copper,§ nickel-gold,|| ¶ platinum-copper,¶ and platinum-nickel.¶ It is indeed gratifying that the present authors have extended the earlier work on the oxidation of platinum-nickel alloys.¶

We have recently completed extensive research on the oxidation of copper-palladium and copper-platinum alloys. The details of the findings will be published shortly. During the course of this investigation, Professor Wagner kindly furnished us with details of the theoretical considerations on the oxidation of alloys to which the authors have referred. It is unfortunate that Professor Wagner's paper has never been published. Careful study of his unpublished work indicates that Kubaschewski and v. Goldbeck have misinterpreted the meaning and intent of the term "corrosion constant". Let us consider the model upon which Wagner based his theoretical considerations. This is shown in Fig. A. The NiO scale layer is assumed to grow by the diffusion of Ni^{++} ions by a vacancy mechanism from the scale/metal interface to the scale/oxygen interface where the reaction with oxygen occurs. It is assumed that the scale contains no noble metal in solid solution or otherwise. The oxidation to NiO tends to deplete the alloy of nickel at the scale/alloy interface. This sets up a concentration gradient within the alloy which causes nickel to diffuse to the interface for further oxidation. Correspondingly, there is also a backward diffusion of platinum towards the interior of the alloy. It is also assumed that the alloy oxidizes parabolically. A necessary condition for parabolic behaviour is that the concentration of nickel at the scale/metal interface be constant with time. This, Wagner has termed the "stationary concentration", and it is indicated in Fig. A as N_s (mole fraction Ni). Wagner was able to show that as long as N_s was greater than about 10^{-2} the alloy would oxidize at a rate less than that of the pure metal. N_s is a function of the initial alloy composition N_0 and γ , where γ is the ratio of the diffusion coefficient in the alloy phase (assumed independent of concentration) and the "corrosion constant" of the pure metal. For a given value of γ , N_s

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† G. Tammann and H. Rienäcker, *Z. anorg. Chem.*, 1926, **156**, 261.

‡ J. A. A. Leroux and E. Raub, *Z. anorg. Chem.*, 1930, **188**, 205.

§ E. Raub and M. Engel, *Vorträge der Hauptversammlung Deut. Ges. Metallkunde*, 1938, 83.

|| C. Wagner and K. Grünwald, *Z. physikal. Chem.*, 1938, [B], **40**, 455.

¶ O. Kubaschewski, *Z. Elektrochem.*, 1943, **49**, 446.

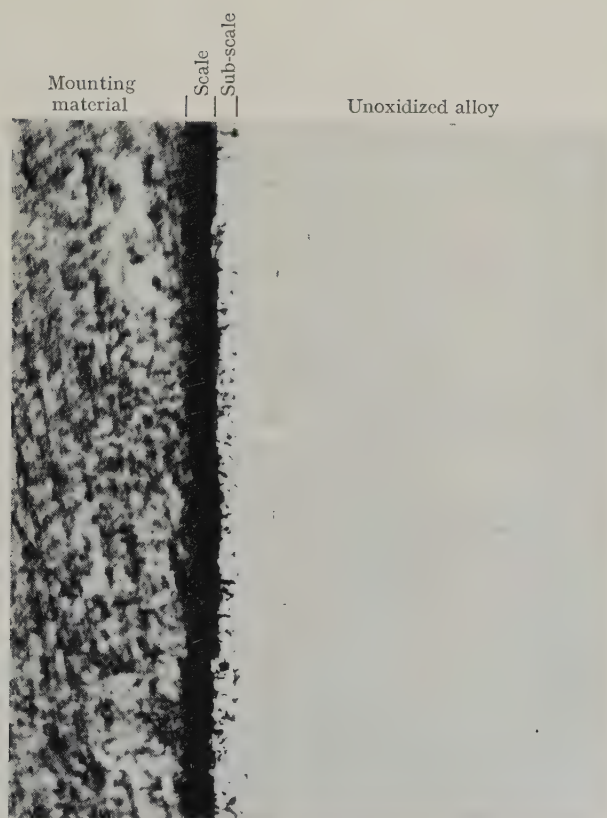


FIG. C.—Photomicrograph of Ni-15 at.-% Pt Alloy Oxidized at 926° C. for 7.47 hr. Atmosphere: oxygen, 760 mm. Hg. $\times 200$. (Thomas.)

decreases linearly with decreasing N_0 . Thus for large values of γ , diffusion in the alloy phase is rapid enough to maintain N_s at a value greater than 10^{-2} over a large range of N_0 . As the initial platinum content is increased (i.e. N_0 decreased), N_s decreases until a value of about 10^{-2} is reached, up to which point the oxidation rate of the alloys is the same as that of pure nickel, but with further increase in initial platinum content N_s falls below about 10^{-2} and oxidation is slower. In the first case, diffusion in the scale is rate-determining, and in the latter case diffusion of nickel in the alloy phase is rate-determining. This situation is illustrated in Fig. B.

Referring again to Fig. A, it is to be noted that $\Delta\xi^*$ is the displacement of the scale/metal interface from the position of the initial alloy surface. This choice of reference frame is convenient in formulating the functional relationship between N_0 , N_s , K_0 , and D , where $K_0 = \frac{(\Delta\xi^*)^2}{2t}$ and D is the diffusion coefficient in the alloy phase. In the case of the oxidation of pure nickel,

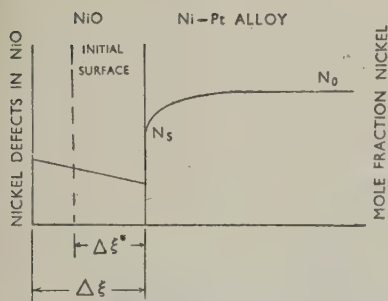


FIG. A.—Wagner's Model for Oxidation of an Alloy of a Base Metal and a Noble Metal as applied to the Ni-Pt System.

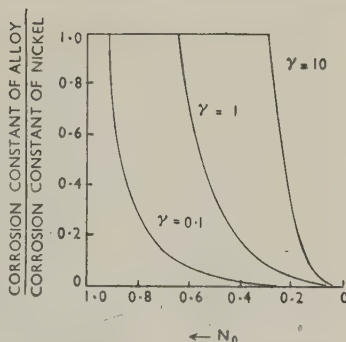


FIG. B.—Corrosion Constant of Nickel Alloys as a function of initial nickel concentration. (After Wagner.)

$\Delta\xi^*$ is the thickness of nickel which has been oxidized and is related to the thickness of the oxide, $\Delta\xi$, by equation (6) of the paper :

$$\Delta\xi^* = \phi \Delta\xi$$

where ϕ is the reciprocal of the Pilling and Bedworth critical density ratio. The authors have given the equation :

$$K_0 = k\phi^2$$

where

$$K_0 = \frac{(\Delta\xi^*)^2}{2t} \text{ and } k = \frac{(\Delta\xi)^2}{2t}$$

for conversion of the oxidation constant based on scale thickness to that based on displacement of the scale/metal interface. In applying this to alloys the authors have modified ϕ by dividing by the volume fraction of nickel in the alloy to "allow for the dilution or 'expansion' of the nickel". This operation would be valid only if, as the scale/metal interface moves inward, the nickel atoms remained stationary in the metal lattice until oxidized to NiO and the platinum completely *disappeared* from the system. The operation would only be approximately valid if the platinum were trapped in the oxide, but this is contrary to the assumptions of the theory. Therefore, if the simple model shown in Fig. A be accepted, the quantity ϕ should not be altered for

the alloys, since if a volume, v , of nickel is removed from the surface of an alloy by selective oxidation, the alloy will shrink by an equal amount, v , if Vegard's rule is obeyed. Deviations from Vegard's rule are not usually large. The values of K_0 shown in Table II of the paper (p. 261) therefore suffer from lack of physical significance and cannot be used, as in Fig. 1 of the paper, to compare with Wagner's theory. If Wagner's theory is valid, then the dependence of the parabolic rate constant upon composition will have the same form whether it is based on weight change, scale thickness, or scale/metal-interface movement. A plot of the experimental rate constant k' against platinum content does not have the shape predicted by the theory as in Fig. B, since k' falls off gradually with increasing platinum content. Consequently, either the conditions of the theory are not met, or the theory itself is wrong.

In connection with our work on the oxidation of copper-palladium and copper-platinum alloys (which are comparable systems), it is pertinent to point out that all alloys which formed oxide scales (as opposed to thin films) also formed a sub-scale which in many cases was quite thick. In addition, we have oxidized a nickel-platinum alloy containing 15 at.-% platinum at temperatures of 850°–1000° C., and found that here, too, a sub-scale is formed (see Fig. C, Plate CXII). The oxide of the scale and of the sub-scale is NiO. We have measured the thickness of the scale and the sub-scale and find that the sub-scale thickness is from $\frac{1}{2}$ to $1\frac{1}{2}$ times the scale thickness. Although the data scattered too much to establish the exact rate law, it appears that the scale and sub-scale both follow the parabolic law. Thus it seems that the simplifying assumptions made in the development of the theory are not realized and the conclusions drawn by the authors concerning the mechanism of oxidation must be altered to account for sub-scale growth. In order to do this, it is necessary to consider additional factors in the scheme of the oxidation process. These are: (1) the dissociation of NiO at the scale/sub-scale interface, (2) the diffusion of the O²⁻ ions thus formed back into the alloy phase where reaction to NiO and precipitation occurs to form the sub-scale.

We would like to ask the authors if they have any data concerning the presence of platinum in solid solution in the NiO scale. We have observed that palladium and platinum are present in solid solution in Cu₂O formed on copper-palladium alloys and platinum-copper alloys, respectively.

The AUTHORS (*in reply*): We are very grateful to Dr. Thomas for having studied our paper in detail and for elaborating upon Professor Wagner's theory. We have also received a valuable private communication from Professor Wagner* which refers partly to the same points. Dr. Thomas is undoubtedly justified in his objections to our interpretation of Wagner's theory, with regard to the modification of the quantity ϕ by dividing by the volume fraction of nickel. This means that all the values of K_0 in our Table II (p. 261) should be multiplied by the square of the volume fraction of nickel in order to obtain the true "corrosion constants". Then, of course, as suggested by Dr. Thomas, our measurements either disprove Wagner's theory, or do not meet the conditions on which the theory depends. There are several possible causes for this: (i) the existence of a sub-scale formation, as observed by Dr. Thomas; (ii) the diffusion rate of nickel in platinum may not be independent of concentration, as was assumed; (iii) the assumption that nickel oxide in equilibrium with nickel contains nickel vacancies may be inapplicable; or, lastly, (iv) the affinity between nickel and platinum is relatively great and the change in the oxygen dissociation pressure of nickel oxide with the platinum content cannot be neglected. This last possibility, namely the existence of a free energy of alloy formation, may well interfere with Wagner's theory,

* Private communication, 5 August 1950.

as was suggested in the paper. Its effect is not likely to be very great, however, if the nickel-platinum system is regular. To settle the matter, however, some additional experimental information is required, which is not yet available, regarding the concentration dependence of the diffusion of nickel in platinum; the relationship between the electrical conductivity of NiO and its oxygen pressure (as was investigated by Wagner and Koch* for CoO); and the free energy of formation of nickel-platinum alloys (cf. work on copper-platinum alloys †). Unfortunately, we did not examine the oxide layers microscopically. The photomicrograph supplied by Dr. Thomas is therefore very welcome and may provide a further clue to establishing the mechanism of oxidation.

There is no doubt that our data conform to a constant K_0 when interpreted as we have done, and there are other systems for which the results can be evaluated in the same way, e.g. the oxidation of copper-silver alloys in Raub and Engel's ‡ paper. Any general theory must account for this fact. Dr. Thomas has mentioned one possible explanation, namely, that platinum is trapped in the oxide. This possibility must be borne in mind, though there are several objections to this mechanism. It is inconsistent for instance § with the assumption of diffusion of Ni^{++} ions and electrons in NiO. In accordance with Pfeil's experiments|| on oxidation, using inert indicators, one would expect the platinum to remain at the boundary of the alloy and oxide phases.

Rather than extend this discussion with our present incomplete knowledge, it appears better to await Dr. Thomas's publication of his research on the oxidation of copper-palladium and copper-platinum alloys, and the paper promised by Professor Wagner § on the theoretical analysis of the diffusion processes determining the oxidation rate of alloys. Both these publications will doubtless contain much valuable information on the problem under consideration and will probably entail a discussion of our own results.

There remain only a few additional remarks to be made:

In reply to Dr. Thomas's last question, we have no data concerning the presence of platinum in solid solution in the NiO scale.

For NiO, Hedvall's ¶ density of 7.45 was used in the paper. Wagner § prefers the X-ray density, which is 6.84.

We wish to make it clear that the values of Δm given in our paper are in terms of the mass of nickel oxide and not the actual weight increases.

There is one misprint in the numerical equation on p. 262; it should read 4.15×10^{-9} in place of 4.15×10^{-10} .

* C. Wagner and E. Koch, *Z. physikal. Chem.*, 1936, [B], 32, 439.

† F. Weibke and H. Matthes, *Z. Elektrochem.*, 1941, 47, 421.

‡ E. Raub and M. Engel, *loc. cit.*

§ Private communication, 5 August 1950.

|| L. B. Pfeil, *J. Iron Steel Inst.*, 1929, 119, 501.

¶ A. Hedvall, *Z. anorg. Chem.*, 1915, 92, 381.

DISCUSSION ON THE PAPER BY DR. A. H. SULLY, DR. H. K. HARDY, AND MR. T. J. HEAL: "THE ALUMINIUM-TIN PHASE DIAGRAM AND THE CHARACTERISTICS OF ALUMINIUM ALLOYS CONTAINING TIN AS AN ALLOYING ELEMENT."

(*J. Inst. Metals*, this vol., p. 269.)

PROFESSOR CYRIL STANLEY SMITH,* Sc.D. (Honorary Corresponding Member to the Council for the U.S.A.): Two investigations † ‡ dealing with the distribution of tin in aluminium-tin alloys have recently been carried out at the University of Chicago.

In a casting of an aluminium-rich aluminium-tin alloy, the tin-rich liquid will tend to form a continuous network around grain edges and between the branches of dendrites. On annealing, however, it will collect under the influence of surface tension into essentially spherical drops when isolated within the grains, while along the grain edges it will form a continuous network of triangular cross-section. Because of this partial isolation of the tin into individual droplets, and because of the lack in a good many of them of nuclei to produce solidification near the freezing point, there may be considerable undercooling. Cooling curves taken on an aluminium-tin alloy containing 10% tin (after annealing the casting for 8 hr. at 480° C.) show that less than one-tenth of the tin solidified above 210° C. and three large spurious arrests appeared at lower temperatures, the largest being at 170° C. In one case a small but definite thermal effect was found as low as 130° C.—after more than 100° C. undercooling. The precise shape of the cooling curve depends on the accidental presence of effective nuclei and their relation to the particular dispersion and connectivity of the particles of liquid phase. It would be interesting to know if the authors have observed such undercooling and spurious thermal arrests, either in their laboratory work or in the commercial casting of these alloys.

The extent to which a molten phase in an alloy penetrates between crystals of the solid phase depends on the relative values of the energies of the various interfaces involved, and is highly sensitive to the composition of the liquid. In aluminium-tin alloys, at a sufficiently high temperature the liquid is aluminium-rich and penetrates completely between aluminium grains, for the liquid/solid interface energy is less than half the grain-boundary energy. As the temperature is lowered, the liquid becomes progressively more and more rich in tin, the energy of the liquid/solid interface increases, and with it the "dihedral angle". This has a marked effect on the hot shortness of alloys either as cast or after working. This is referred to in my discussion of the paper by Crowther,§ wherein the authors' new data for the liquidus in the

* Director, Institute for the Study of Metals, Chicago, Ill., U.S.A.

† K. K. Ikeuye and C. S. Smith, *Trans. Amer. Inst. Min. Met. Eng.* (in *J. Metals*), 1949, 185, 762.

‡ C.-C. Wang and C. S. Smith, *Trans. Amer. Inst. Min. Met. Eng.* (in *J. Metals*), 1950, 188, (1), 136.

§ *J. Inst. Metals*, this vol., p. 726.

binary aluminium-tin system are used to plot a curve of the relative interface energy as a function of composition.

The AUTHORS (*in reply*): We are indebted to Professor Smith for the interest which he has taken in our paper.

Undercooling or spurious arrests were not detected in the course of our thermal analysis of these alloys. Our failure to observe these phenomena is probably due to the fact, mentioned by Professor Smith, that it is only on annealing that isolated pools of tin eutectic form within the grains and lack nuclei for solidification. Our thermal analysis was conducted entirely on cast alloys and in these, as Professor Smith states, the tin-rich liquid forms a continuous network around the grain edges and in the interdendritic regions. Isolated pools, lacking solidification nuclei, are therefore absent.

We have studied with particular interest the papers by Professor Smith and his co-workers to which he refers and have found the data presented, on the variation of interfacial energy with temperature, of great assistance in explaining the microstructural changes which take place in these alloys on heating at temperatures above the eutectic temperature. We can confirm that as the solid/liquid interfacial energy increases, and with it the dihedral angle, the consequent agglomeration of the tin-rich phase exercises an important influence on the properties of these alloys at elevated temperatures. In work subsequent to that described in the present paper, which it is hoped to publish, it has been shown that the ductility of these alloys at elevated temperatures may be improved even at quite high tin contents, by a suitable combination of working and annealing.

Opportunity may be taken of correcting a small but important omission from Fig. 3 (p. 274), which illustrates the thermal-analysis furnace. A radiation shield is not shown in the diagram, but a graphite crucible of the same size as that holding the metal was always used. The base was drilled to pass the thermocouple sheath and stirrer, and this crucible was placed on the lid of the melting crucible in an inverted position. By this means the radiation losses from the thermocouple sheath were prevented from affecting the measured temperature of the metal. The same e.m.f. values were obtained on pure aluminium or pure tin as were given by the standard calibration technique using a large quantity of metal.*

* W. F. Roeser and H. T. Wensel, *Temperature Measurement and Control in Sci. and Ind.* (*Amer. Inst. Physics*), 1941, 284.

JOINT DISCUSSION ON PAPERS BY MRS. M. D. EBORALL: "GRAIN REFINEMENT OF ALUMINIUM AND ITS ALLOYS BY SMALL ADDITIONS OF OTHER ELEMENTS"; BY MR. A. CIBULA: "THE MECHANISM OF GRAIN REFINEMENT OF SAND CASTINGS IN ALUMINIUM ALLOYS"; AND BY MR. A. CIBULA AND MR. R. W. RUDDLE: "THE EFFECT OF GRAIN-SIZE ON THE TENSILE PROPERTIES OF HIGH-STRENGTH CAST ALUMINIUM ALLOYS."

(*J. Inst. Metals*, this vol., pp. 295, 321, 361.)

MR. A. CIBULA*: Since the work was published, I have been able to identify tantalum carbide (TaC) particles in an aluminium-0.1% tantalum alloy, by acid extraction and subsequent X-ray examination of the segregate in a centrifuged specimen of the alloy.

MR. R. W. RUDDLE*: Since the papers were submitted for publication, it has been suggested to Mr. Cibula and myself that the relationship between tensile strength and grain-size, described in our joint paper, might be affected by the rate at which the test-bars were poured. Some further work was therefore carried out by Mr. A. L. Mincher in order to check this point. Melts of the aluminium-4½% copper alloy were made, using the same technique as before, and were poured into test-bars from various temperatures. Two D.T.D. bars were poured from each melt, one at a fast rate (3-5 sec./bar) and the second at a relatively low rate (30 sec./bar). The grain-sizes, densities, and mechanical properties of the bars were determined after heat-treatment as described in our paper. The results showed that the increase in grain-size with casting temperature is substantially independent of the pouring rate. However, it was found that the soundness of the bars was quite markedly affected by pouring rate (Fig. A), the fast-poured bars having almost twice as much porosity as those poured slowly. The reduction in porosity caused by slow pouring is thought to be due to improved mass-feeding during solidification as the result of the steeper temperature gradients produced. Micro-examination showed that the pouring rate does not affect the form and distribution of the voids, which are therefore solely dependent upon grain-size. This fact is reflected in the mechanical properties obtained from the bars; the bars poured slowly had slightly better mechanical properties than those poured fast, but the difference is small compared with the effect of grain-size. Figs. B and C show the U.T.S. plotted against pouring temperature and grain-size, respectively. The dotted lines are the comparable curves taken from our paper (curves obtained using an intermediate pouring

* Remarks made in introducing the papers for discussion at the Annual General Meeting of the Institute in London, March 1950.

rate of 10 sec./bar). The conclusion drawn from Mr. Mincher's work is that the tensile properties of test-bars in this and similar alloys are mainly affected by the form of the shrinkage voids and to a much lesser extent by their amount.

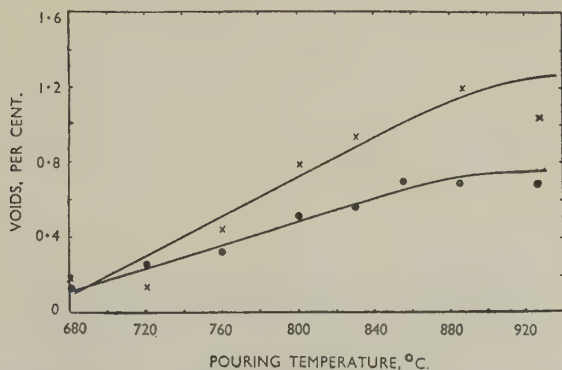


FIG. A.—Variation of Percentage Voids with Casting Temperature of Fast and Slowly Poured Test-Bars. (Ruddle.)

× — × Pouring time 3-5 sec.
• — • Pouring time 30 sec.

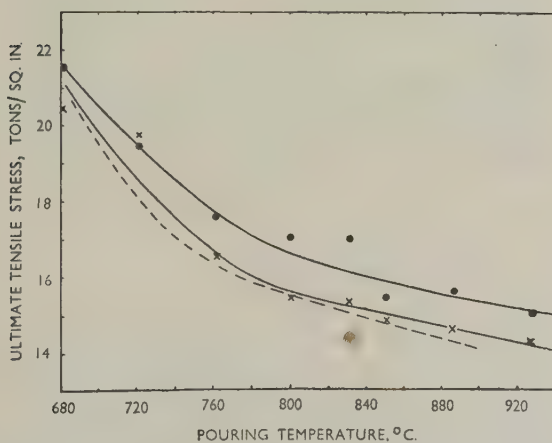


FIG. B.—Variation of U.T.S. with Pouring Temperature. (Ruddle.)

× — × Pouring time 3-5 sec.
• — • Pouring time 30 sec.
--- Previous work (*J. Inst. Metals*, this vol., p. 361).

MR. A. W. BRACE,* A.I.M. (Junior Member): The work is of great theoretical and practical interest. There are several points in relation to the application of the results which might usefully be made clearer. The study of the effect of grain-refining elements had obviously to be based on the

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percentage by weight of a given element added to the metal. The investigations, however, show that it is not the total weight of the elements present that is of major importance, but the amount of carbides formed. It is difficult to judge whether the actual merits of these elements can be assessed on the basis of the weight required to produce a given grain-size, since it may be that carbides are less readily formed in some of the heavier metals. It would be interesting to know whether the authors have attempted to determine how much of a carbide of an element is necessary to produce grain refinement. A further point which is not clear is whether the hardeners used contained carbides or whether these were formed by reaction with carbon already present in the metal. Once this information was available it might be possible to increase appreciably the efficiency of grain-refining elements.

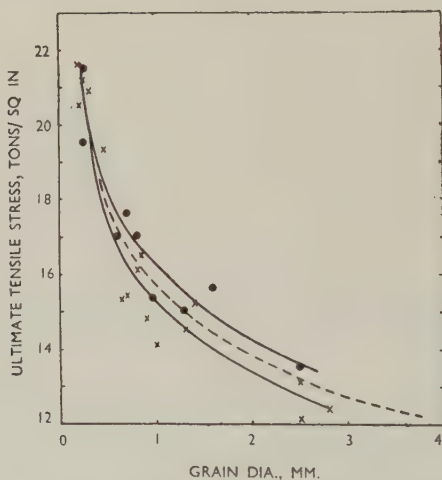


FIG. C.—Variation of U.T.S. with Grain-Size. (*Ruddle.*)

- ×——× Pouring time 3–5 sec.
- Pouring time 30 sec.
- — — Previous work (*J. Inst. Metals*, this vol., p. 361).

It has been shown in this work that the passage of gas or turbulence of any kind could precipitate these nuclei and therefore remove them from any effective role. In commercial practice it is often necessary to treat the metal in some way to remove excess dissolved gas, and the methods commonly used involve the passage of either chlorine gas or nitrogen used in conjunction with a flux cover. It seems possible, therefore, particularly in alloys of the LM-7-M type where titanium had been deliberately added, that degassing could remove the effectiveness of grain refinement, thus resulting in a grain-size not much better than that of the alloy without such an addition. If this is so, it would appear interesting to investigate the possibility of adding the grain refiner after gas removal, or preferably combining grain refinement with gas removal by using it in conjunction with a carbon-bearing gas.

Many alloys contain a certain amount of titanium either as an impurity or as a deliberate addition, and it would be useful to know whether the authors have investigated the effects of adding another grain refiner such as boron to a melt already containing titanium. In such a case the practical man would



FIG. D.—Chill-Cast Copper-Iron Alloy. $\times 200$. (*Clarebrough.*)

be glad to know if the effect was cumulative or independent of the presence of another element.

MR. C. S. CAMPBELL,* M.A. (Member): Regarding Section IV of Mr. Cibula's paper, the identification of titanium and tantalum carbide particles is very interesting, but it is unfortunate that in the case of tungsten and of molybdenum one has, in the absence of experimental work, to rely on indirect evidence of stability and structure. Our knowledge of the thermodynamics of these systems is, as yet, limited, but the present evidence would not necessarily support the stability of these particular carbides in liquid aluminium.

We have recently measured the free energy of formation of aluminium carbide at 920° C. and obtained a value of -33 kg.-cal., or -11 kg.-cal./g.-atom of carbon. An activity of 0.01 for the grain-refining element in the concentrations employed would not be unreasonably low, so that at 1000° K. a grain-refining carbide should have a free energy of formation of -20 kg.-cal. or more. The evidence available would not suggest that tungsten or molybdenum carbides have such a free energy. The highest value recorded for the heat of formation of tungsten carbide is 8.4 kg.-cal., and the entropy of formation of these interstitial carbides is believed to be negative. While the melting point is high, it should be compared with the melting point of the metal.

In commercial alloys, silicon is usually present in greater amount than the grain-refining element, and in these cases it should be borne in mind that the free energy of formation of silicon carbide at the temperatures in question is -24 kg.-cal.

MR. L. M. CLAREBROUGH,† B.Met.E., M.Eng.Sc. (Junior Member): I was interested to read in Mrs. Eborall's paper of grain growth in cast aluminium-titanium alloys, as I have made similar observations with copper-iron alloys. Fig. D (Plate CXIII) is a photomicrograph of a chill-cast copper-iron alloy containing approximately 0.5 wt.-% iron. Here, as in the aluminium-titanium alloys, there is marked coring and the dendrites as well as the grain boundaries are revealed by etching. The final grain boundaries including angles of 120° appear to be entirely independent of the dendritic structure, and this result must be caused by boundary migration after solidification. Thus this grain-growth phenomenon is not peculiar to aluminium alloys.

DR. M. L. V. GAYLER (Member): Mrs. Eborall has shown that a peritectic reaction is not essential for grain refinement and that, in the case of aluminium-titanium alloys, the method of addition of titanium was a factor affecting the refinement. One of the theories put forward for the modification of aluminium-silicon alloys is the presence of a peritectic reaction in the aluminium-silicon-sodium system. Recently Scheil and Zimmermann‡ found that modification of aluminium-silicon alloys is produced only when sodium is added "as metal" and not when added in the "combined state", i.e. as a ternary compound. Mrs. Eborall's conclusions indicate that modification of aluminium-silicon alloys by sodium is not due to the peritectic reaction in the ternary system; thus providing further evidence that the above theory of modification does not hold good.

DR. V. KONDIC,§ B.Sc. (Member): Mr. Cibula's paper is a major event in that field of physical metallurgy dealing with the problem of cast structures.

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† Research Officer, Division of Tribophysics, C.S.I.R.O., University of Melbourne, Australia.

‡ E. Scheil and R. Zimmermann, *Z. Metallkunde*, 1949, 40, (1), 24.

§ Lecturer in Industrial Metallurgy, Birmingham University.

An important observation recorded in the paper is that the degree of undercooling of liquid solutions solidifying under a certain rate of cooling, increases with increase of solute. This feature has been confirmed at Birmingham University and found to be quite general in a number of other binary systems. I should like to discuss Mr. Cibula's interpretation of this observation. Briefly, it is suggested that the cooling curves obtained do not provide an answer to the question of absolute undercooling, i.e. the temperature of formation of the first crystallites, but instead that the undercooling temperature measured is merely a consequence of solute atoms restricting the growth of the first crystals formed in the solution, thus allowing the rest of the liquid to undercool still further.

That explanation can be challenged on both experimental and theoretical grounds. Experimentally, it suggests that the amount of heat liberated by the formation of the first crystals formed is so small that the total heat liberated before these crystals are effectively blanketed by solute atoms produces no detectable effect on the cooling curve under the experimental conditions used by the author. If so, could Mr. Cibula tell us what happens to that heat? Furthermore, the experimental evidence obtained by placing the hot junction of the thermocouple at the very surface of the casting reveals that the degree of undercooling increases with the percentage solute. Thus, whilst the adsorption theory could be used to account for the delayed formation of nuclei deeper in the melt, it cannot explain the mechanism of the formation of nuclei at the surface.

On the theoretical side the explanation in terms of adsorption and undercooling of the origin of cast structure of solid solutions could be argued against on the following grounds. If a crystal is prevented from further growth by the presence of a certain amount of adsorbed solute atoms, then there should be a critical percentage of solute atoms which is just sufficient to produce this effect. In other words, if a small percentage of solute is already effective in blanketing a nucleus from further growth, why should a slightly larger amount of solute lead to greater undercooling? A similar question suggests itself from the author's finding that the presence of suitable foreign nuclei completely inhibits the undercooling. Why do not foreign nuclei at the surface of the casting, according to the adsorption theory, lose their power for further growth once a small amount of solute has crystallized upon such nuclei?

Instead of the assumption made in the adsorption theory that an increasingly finer equi-axed structure of solid solutions is caused by the restricting actions of solute atoms on crystal growth, it seems to me that a more reasonable assumption is that the absolute undercooling which increases with the percentage solute gives rise to a larger number of nuclei and thus a finer cast structure. Incidentally, in this connection, I fail to see what justification the author had for using Tammann's classical postulates to support the adsorption theory. Tammann's findings do suggest, however, that the number of nuclei increases with the degree of undercooling, and this factor alone would explain the grain-refining effect of solute atoms.

It seems to me, therefore, that there is no need to resort to the adsorption mechanism to account for either the greater undercooling or the increasingly finer structure with increasing percentage of solute. Where the adsorption theory does come in, as used by Dr. Northcott, is in explaining the transition of columnar to equi-axed structures. In this respect I consider that the author was right in invoking the adsorption theory to account for some of the results observed.

The AUTHORS (*in reply*): With regard to Dr. Gayler's comments, we think that the modification of the aluminium-silicon alloys by sodium is not strictly analogous to the grain refinement of aluminium by titanium. Scheil and

Zimmermann * added sodium either as metal or as NaAlSi_4 and were able to observe particles of this compound in the structure when modification had failed. After long soaking of alloys treated with NaAlSi_4 , however, the sodium entered the alloy and modification occurred; the effect seems to have been due to slow reaction between the compound and molten metal, and the possibility of a peritectic reaction during solidification being responsible for this particular phenomenon is not affected.

Mr. Clarebrough's comments are noted with interest; attention had also been drawn to a similar effect encountered by Dr. Voce in copper-base alloys during some earlier work carried out at the B.N.F.M.R.A.

We fully agree with Dr. Kondic that there is little need to resort to the adsorption mechanism to explain our observations; indeed, it was mentioned once only, with reference to work by Dr. Northcott, and we cannot understand, therefore, Dr. Kondic's criticisms of our alleged use of the theory.

The explanation we put forward for the undercooling and refining effects produced by the solution of copper, nickel, and some other elements in the pure aluminium, was based on the concentration-gradient theory which, as described both in our paper and, more fully, in the references quoted therein, is quite different from the adsorption theory. The concentration-gradient theory proposes that the growing dendrites in a cast alloy are surrounded by a layer of liquid metal which (in an aluminium-base hypoeutectic alloy) is enriched in solute atoms, owing to the high aluminium content of the solid deposited from the melt, and has a correspondingly low liquidus temperature. The rate of growth of the dendrites is thus controlled by the rate at which the solute atoms can diffuse away from this enriched layer; if solidification of the dendrites is hindered to such an extent that the liberation of latent heat is less rapid than the abstraction of heat by the surrounding metal and mould material, the liquid metal in front of the enriched layer undercools and new crystallites can form there.

We cannot understand Dr. Kondic's suggestion that "the absolute undercooling which increases with percentage solute gives rise to a larger number of nuclei and thus a finer cast structure". An increase in "absolute undercooling" required for the formation of crystallites must surely mean, in more precise terms, that the rate of nucleation at a given degree of undercooling is *reduced*. How can this produce a *larger* number of nuclei and a *finer* structure?

The observed increase in undercooling and reduction in grain-size as the concentration of solute was raised, can be explained quite simply, however, by an extension of the theory described above.

The initial undercooling at the surface of a casting reaches a maximum not when the first crystallites are formed, but when the liberation of latent heat becomes as rapid as the abstraction of heat by the mould, that is, when a certain rate of solidification is attained. In high-purity aluminium, crystal growth can only be slightly impeded by concentration gradients, and the critical rate of solidification is probably reached very soon after the first crystallites are formed; the minimum temperature before rapid and complete recalescence begins must, therefore, be almost identical with the temperature at which nucleation occurs. In aluminium-copper alloys, on the other hand, crystal growth from the surface of the casting is hindered by concentration gradients, to an extent depending on the rate of cooling and the concentration of solute. The rate of solidification (i.e. the product of the area of the solidification front and its linear velocity) attains the critical value, therefore, only after the first crystallites have grown appreciably and the temperature has fallen well below the nucleation temperature.

Thus, undercooling is increased and prolonged, and recalescence is retarded,

* *Loc. cit.*

by the presence of a solute. These effects should increase with copper content, because of the greater difference between the compositions of the liquid and solid metal; when the concentration of copper is large enough, recalescence is sufficiently retarded to allow undercooling to spread into the interior of the casting where new grains can then form, their number increasing with the degree of undercooling as described by Tammann. The increase of undercooling with copper content is limited, however, by the marked rise in the nucleation rate which occurs when a certain degree of undercooling is attained. This prevents undercooling from exceeding a certain limiting range depending on the rate of cooling; it is to be expected, therefore, that an increase in the percentage of copper beyond a certain value would produce little more effect.

All the observations described in the paper can be explained in this way, and although the presence of a solute may possibly increase the undercooling required for the formation of a crystallite, as suggested by Dr. Kondic, we do not believe that any conclusion about this can be drawn from our results.

Mr. Brace has suggested that the carbon of the nuclei in fine-grained aluminium alloys may be derived either from the alloy to which the refining element is added or from the hardener containing the refiner; our experiments have confirmed both these suggestions. The marked reduction in grain-size produced by the addition of high-purity aluminium to a coarse-grained aluminium-titanium alloy (described in Cibula's paper) indicates that part of the carbon is derived from the casting alloy itself, and we have also identified titanium carbide particles in an aluminium-titanium hardener alloy, by the technique of centrifuging followed by X-ray examination.

The amount of carbide required to produce adequate grain refinement has only been estimated for an alloy containing titanium; of the 0.1-0.15% titanium added as a hardener to alloys cast at temperatures up to 750°-800° C., only one-tenth or less was in the form of titanium carbide. The minimum concentration of dissolved titanium in equilibrium with solid titanium carbide in molten aluminium, has been estimated (from the concentration required to produce very slight refinement) to be less than 0.003%. Consequently about 0.01%-0.02% titanium should produce adequate refinement if it is all present as a nucleating compound. We hope to describe in a future paper the results of work on the addition both of carbon and of boron to alloys containing titanium and other grain-refining elements.

We agree with Mr. Brace that the grain-refining addition is best made just before casting, if a gas-free hardener is used, but quite satisfactory results are obtained by adding the hardener to the charge when melting the alloy, if subsequent overheating is avoided. The titanium may become ineffective, however, after remelting the metal several times, holding the melt for long periods at a low temperature, or prolonged treatment with nitrogen, particularly if a flux is used. We doubt whether the use of carbon-bearing gases would prevent grain-coarsening. There is the difficulty of making carbon react with molten aluminium, unless an active flux or a high temperature is used, and the problem of preventing the solid particles of carbide from rising to the surface of the melt with the gas bubbles.

We wish to thank Mr. Campbell for giving his recently determined value of the free energy of formation of aluminium carbide. The values of free energies of formation quoted in Table VIII of Cibula's paper (p. 343) are those available in the literature when, in order to continue our experiments, we had to consider which compounds were likely to exist as nuclei in molten aluminium. The data indicated that, in general, only the carbides have a high enough stability compared with the stability of the corresponding aluminium compound. As shown in the paper, this indication agreed well with the known grain-refining properties of the transition metals and the structures of their

carbides, and subsequent experiments confirmed the existence of carbides in the fine-grained alloys of two of these transition metals.

In the case of molybdenum, the published value of the stability of the carbide was not consistent with the presence of the compound in molten aluminium; Mr. Campbell has pointed out that the same is true of tungsten carbide, if the most recent value is compared with his value for aluminium carbide. We find it difficult to reconcile these data with the published data of the carbides of the other transition metals and the observed carbide-forming properties of these metals when present in steel; tungsten and molybdenum, for example, are noted * as strong carbide-formers, whereas neither aluminium nor silicon appear to form a carbide in steel. It is possible that the apparent disagreement may be explained by taking into account the free energies of solution of the metals in molten iron but, unfortunately, these data are not known. We agree that there are probably considerable errors in the published data on the free energies of formation of the carbides, for the reported values often vary widely. For these reasons we doubt whether it is justifiable to rely on the data to obtain more than a general indication of the stability of the carbides.

* J. M. Hodge and E. C. Bain, *Metals Handbook (Amer. Soc. Metals)*, 1948, p. 453.

SYMPOSIUM ON METALLURGICAL ASPECTS OF THE HOT WORKING OF NON-FERROUS METALS AND ALLOYS.*

MORNING SESSION (Papers Nos. 1225-1228).

DR. C. J. SMITHELLS, M.C., F.I.M.† (Vice-President) (*Rapporteur*), said he had great difficulty in finding some factors which appeared common to the problems of hot rolling, extrusion, and forging. The factor to which all the authors drew attention was the necessity for having a satisfactory cast structure, free from porosity and internal stresses, and with a suitable grain-size, as a starting point for all hot-working operations. There was no doubt that a number of the problems associated with the hot working of aluminium and magnesium were closely connected with the structure of the cast block, and that, given a satisfactory cast billet, many of the difficulties disappeared.

Dr. Smithells then summarized the main points of the papers one by one.

MR. R. CHADWICK,‡ M.A. (Member), said that one of the authors of the series of papers to be presented in the afternoon had defined hot working as working at temperatures appreciably above the recrystallization temperature. In the light alloys it was clear that what was termed "hot working" might or might not involve recrystallization. Moreover, recrystallization in many of the alloys concerned was a very complex phenomenon, so that the actual changes occurring were seldom fully understood. Only, perhaps, with super-pure aluminium were conditions at all similar to those in the more familiar copper alloys.

Small amounts of elements such as iron, silicon, and manganese exerted a disproportionately large effect upon the recrystallization of aluminium. In commercial aluminium containing silicon and iron, the annealing temperature was raised and the grain-size of cold-rolled and annealed sheet was refined, if the ingot was hot rolled at a high temperature, i.e. 500° C. Spillett § had shown, and he himself had confirmed, that a similar effect resulted from an annealing or soaking treatment at 500° C., of the hot-rolled strip. Kasz and Varley's suggestion that when the brittle β (Fe-Si) phase was broken down by hot and cold rolling the ultimate particles interfered with recrystallization, was scarcely plausible. It seemed more likely that the temperature of recrystallization was raised by taking the alloying elements into solid solution before cold rolling. Whether, however, the solid solution itself had a higher recrystallization temperature, as suggested by Dr. Richards and himself,|| or whether, as Beck had suggested,¶ the very fine precipitate formed by the

* Discussion at the Annual General Meeting, London, 30 March 1950.

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§ E. E. Spillett, *J. Inst. Metals*, 1943, **69**, 149.

|| R. Chadwick, T. Ll. Richards, and K. G. Sumner, *J. Inst. Metals*, 1948-49, **75**, 627.

¶ P. A. Beck, *ibid.*, 1151 (discussion).

rejection of supersaturated elements in the cold-worked alloy before recrystallization began interfered with subsequent recrystallization, remained undecided.

Grain-size in the annealing of aluminium depended not so much on the maximum temperature reached in the furnace as on the rate of rise of temperature of the metal through the recrystallization temperature; so that, generally speaking, the higher the furnace temperature, the smaller was the grain-size. If, therefore, the annealing temperature was raised, some refinement of grain might well be expected to result.

When manganese was present, a rise in the annealing temperature or an increase in critical reduction occurred, and some recent work carried out by Hooper and himself* showed the magnitude of this effect. They had not as yet examined aluminium-manganese alloys subjected to different quenching treatments to determine the effect of varying the content of manganese in solid solution, but it was clear from the remarks of Kasz and Varley that it would be of considerable interest to do so.

Smith had stressed the importance of manganese in controlling the incidence of coarse peripheral grain growth in extruded Duralumin-type alloys, and it was clear that the elimination of the range of low critical reductions, in which very large grain growth resulted after small reductions, was the important factor. Hansen had confirmed this,† stating that the critical reduction for Duralumin-type alloys with 0.2% manganese was 4%, while with 0.6% manganese it was 15%. It therefore looked as though manganese was the major factor controlling critical reduction.

In the extrusion of the strong aluminium alloys, long, fibre-like structures resulted from the process of re-absorption of slip bands first described by Carpenter and Elam, although generally in the heat-treated rod the long fibres were apparent only in the macro-examination, higher powers revealing them to be broken down into smaller, more nearly equi-axed units. Unfortunately Smith had shown only the heat-treated condition, but in fact the coarse outer-zone structure which he described was mainly developed by the heat-treatment process itself and, in the extruded condition, the outer zone was often similar in structure to the interior only, rather finer and showed the same (111) and (100) fibre textures. A thin, recrystallized outer zone was sometimes found in the extruded condition, and the extent to which it thickened and spread on heat-treatment varied considerably. In hot rolling the crystals were drawn out in much the same way as in extrusion, but as hot rolling progressed, the temperature usually fell, and this resulted in a degree of cold working which led to recrystallization in the final heat-treatment. The fibre texture therefore disappeared, and a recrystallized structure with random orientation was obtained.

It was evident that a great deal of work would be required to determine all the relationships involved, and that this could only be effectively carried out with better control of press conditions than was at present available. The reheating of extrusions to obtain the necessary mechanical properties did, however, appear to be thoroughly unsatisfactory. The type of operation described by Brauning,‡ in which the rod was brought up to temperature after it left the die and immediately quenched, might result in a valuable improvement.

The observations recorded in Stokeld's paper showed the importance of maintaining the temperature during forging and thus preserving the extruded structure unchanged; in fact, the hot-forging operation might be said to be a

* R. Chadwick and W. H. L. Hooper, *J. Inst. Metals*, 1948-49, **75**, 609.

† M. Hansen, *J. Inst. Metals*, 1948-49, **75**, 1151 (discussion).

‡ B.I.O.S. Final Rep. No. 1656.

continuation of the extrusion process. However, it appeared that this process could not be carried on indefinitely, and Smith had rightly pointed out the importance of the ratio of extrusion diameter to billet diameter. This point could be illustrated by taking a very large billet, say 15 in. in dia., extruding it to 4 in. bar, cutting up the bar into billets, and re-extruding it to, say, $\frac{3}{4}$ in. rod. The 4 in. bar would exhibit the characteristic fibrous structure, but the $\frac{3}{4}$ in. rod would be found to have a coarse, equi-axed structure and low mechanical properties. It was suggested that there was a maximum extent to which the fibres could be drawn out, even when a high temperature was maintained, and that beyond that point the structure became unstable and recrystallized.

MAJOR P. C. VARLEY,* M.B.E., T.D., M.A. (Member), stated that Mr. Chadwick had slightly misunderstood the paper by Mr. Kasz and himself. In referring to the effect of fragmentation of the β (Fe-Si) constituent on the grain-size, they had not intended it to be understood that that effect was also responsible for the other phenomena affected by the temperature of hot working. He was sure that Mr. Chadwick was correct, and that the temperature of recrystallization was raised by taking the alloying elements into solid solution before cold rolling.

MR. W. K. J. PEARSON,* B.Sc. (Member), referred to some remarks made by Kasz and Varley on the effect of block structure in the rolling of aluminium alloys. It was surprising that the block structure did in fact survive through rolling and even through more than one stage of recrystallization. This was brought out by examination of a specimen anodized after rolling and annealing and then examined in polarized light. Groups of grains of similar colour, and therefore of similar orientation, could be traced to the original grains of the cast block.

MR. W. C. F. HESSENBERG,† M.A. (Member), said he would confine his remarks to the paper by Kasz and Varley because it was the one which showed the nicest appreciation of the way in which metallurgy and mechanics were mixed up in these problems.

He commented first on the reference (p. 424) to the work of Baker, Ricksecker, and Baldwin on residual stresses after cold rolling, where he thought there was a slight confusion between the residual stresses left in the slab after rolling and the actual stresses which caused the crocodiling. What Baker and his colleagues had done was to measure the residual stresses and then deduce from those what had been the actual stresses in the metal as it left the rolls, which caused the crocodiling. Those stresses were present to the same extent in hot rolling, the only difference being that the residual stresses were released very quickly at the temperature of hot rolling, so that they could not be measured afterwards. It was significant that Baker's work led directly to the conclusion that, to avoid crocodiling, the roll diameter should be as large as possible in relation to the exit thickness of the rolled slab. Kasz and Varley made the same point at the top of p. 411, where they said that the application of the individual heavy drafts minimized the chances of crocodiling, and again on p. 412, where they referred to the advantage of heavy drafts. For a given size of roll, the heavier the draft, the smaller was the exit thickness, and therefore the larger the ratio of roll diameter to exit size.

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† Head of the Mechanical Working Division, British Iron and Steel Research Association, London.

On p. 423, the authors stated : " Now with such a high coefficient of friction there is a very marked tendency for the metal to stick to the rolls and be torn apart along the centre plane ". Did they think that the coefficient of friction was directly responsible for the sticking or that it was merely a coincidence that the two occurred together? There were no sliding forces involved in the case of metal separating from the roll at the point of exit.

He himself thought that the real origin of crocodiling effects was somewhat different. Supposing that a slab had a centre weakness, and that the weakness was almost complete, so that the slab was really in two halves. The metal lying between the roll surface and the central plane of the slab just before it came out of the rolls had a radius of curvature on its upper surface which was the same as the radius of curvature of the rolls. On the under surface it had an infinite radius of curvature. The moment after it emerged it had to assume the same radius of curvature on both sides. Therefore, it would come to some sort of compromise, with a radius of curvature somewhere between the radius of curvature of the rolls and the infinite radius of curvature on the under surface. It was that adjustment that gave rise to the stresses which, if there were any weakness at the front of the slab, would tend to pull the two halves apart.

There was one other form of cracking, of which the authors were probably well aware, viz. the type consisting of a number of transverse cracks on top of the slab. That was another manifestation of the same effect. If there was no centre weakness but a weakness on the surface, then pulling of the two halves together when they wanted to part caused tension on the surface which might lead to cracking there.

The authors suggested that stagger might be connected with the variation in torque from one roll to another. Did the amount of stagger vary from point to point along the slab? Did the authors put only one plug in each slab, or did they put in a series, and did these all show the same degree of stagger?

MAJOR VARLEY replied that only two plugs were inserted, one at the front and one at the back, and those did show different amounts of stagger as indicated in Table I of the paper. He agreed that it would probably have been better to have inserted plugs all the way along.

MR. N. H. POLAKOWSKI,* Dipl.-Ing., commented on some observations made by Kasz and Varley during their rolling experiments (pp. 416-421) and also on the section " Crocodiling and Edge Cracking " (p. 422).

The asymmetry of deformation of the plugs inserted into the slabs (Figs. 3 and 4, Plates LV and LVI) could be explained if it were assumed that the lower face of the slab was cooler than the upper, as a result of the loss of heat to the roller tables. The resistance to deformation of the metal near to the top would therefore be relatively smaller, and the material would flow more readily. The somewhat greater elongation of the upper portion, as well as the curling up of the front end of the broken-down slab (Fig. 7, Plate LVIII) which might be due simply to differential shrinkage, appeared to support such a suggestion.

This concept seemed to be consistent with the results of torque measurements (p. 420), from which it had been found that the top roll usually transmitted the greater torque. It was reasonable to assume that the coefficient of friction must be appreciably less on the cooler side, i.e. between the slab and the bottom roll, hence accounting for the difference in torque. Some experiments by Emicke and Lucas had revealed that the distribution of

* Research Student, University College, Swansea.

torque between the rolls was reasonably uniform when lubricated strip was rolled. However, when one side of the strip had been degreased, the torque on the appropriate roll increased considerably, while the torque transmitted by the roll on the lubricated side decreased by the same amount, the overall value remaining almost unaltered.

Regarding the reason for crocodiling suggested by Kasz and Varley, he would like only to say that this phenomenon occurred under somewhat similar geometrical conditions in cold rolling as well, when using polished rolls, and in that case friction could not be regarded as a main agent. He believed that a probable explanation could be deduced from the information given in the 1932 May Lecture to the Institute of Metals by Professor Körber * and from the immense amount of data published during the last 50 years, particularly from a recent paper by Mican.†

The suggested explanation could be summarized as follows: when a metallic cylinder, whether hot or cold, was being compressed, it acquired a shape which depended on the initial height:diameter ratio. When this ratio was over 2, a concave contour appeared (two bulges), whereas when it

was less, the contour became convex (single bulge) (see Fig. A). The limiting value 2 was not exact, but could be accepted as a rough approximation.

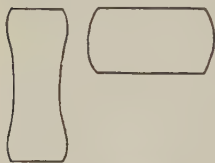


FIG. A. (Polakowski.)

This rule held also when the metal under direct compression formed an integral part of a large mass, as in step-forging or rolling. In this case, instead of the diameter of the cylinder, the minimum horizontal dimension of the tool had to be employed, i.e. the width of die or the length of the arc of contact. Fig. B, series A, showed (upper left-hand section) a simplified version of the conditions described in Kasz and Varley's paper,

when the first 0.2 in. draft was taken on a 6 in.-thick slab, the rolls being 34 in. in dia. The shape factor, which was equal to the ratio slab thickness (h): length of bite (b), was now 3.2, so that there would be a tendency to develop a double barrel, as indicated with light lines. This obviously could not occur in the centre of the slab, but the tendency would remain and result in a distribution of longitudinal stress as shown in the top right-hand diagram. The centre of the slab was in tension ($-$), while the top and bottom were under longitudinal compression ($+$). On considering the front end just leaving the rolls it was clear that the upper and lower edges were extruded forwards while the centre was (relatively) pulled inwards. The resulting couple T_1 acted so as to bring the overlap edges together and so accentuate the "fish-tail" shape.

At the same time any pores and bubbles present around the horizontal plane of asymmetry of the slab, were under the action of the external roll pressure V and the internal tension L . They were flattened and elongated, forming a region of weakness inside the slab, and their position was such that the resistance of the slab to any stresses which might tend to tear the "jaws" apart was considerably reduced. Such stress conditions did actually occur when the slab was thinner, as shown in series B, (Fig. B), which corresponded to a thickness of 2.5 in. and 0.2 in. drafts, the shape ratio being then 1.4. The stresses were now tensile in the upper and lower layers but compressive near the centre, so that the resulting twist T_2 acted in the opposite direction, trying to open the "jaws" (right-hand bottom section of diagram). If the slab did not fail at this moment, which apparently corresponded to the maximum value of T_2 , the possibility of crocodiling was practically avoided,

* F. Körber, *J. Inst. Metals*, 1932, 48, 317.

† G. S. Mican, *Iron Steel Eng.*, 1949, 26, (2), 53.

because later on the value of the twist diminished owing to the decreasing thickness of the material.

MAJOR VARLEY said that it was rather difficult to comment at short notice on this contribution, but it seemed to be a most attractive explanation of the phenomena, and so far as he could see it fitted in with the observations.

MR. J. C. SWAN, M.Met. (Member),* said that in hot rolling his firm did not go above $5\frac{1}{2}$ in. slab, and had never had trouble with crocodiling on pure aluminium. Their difficulties were confined to edge cracking. With

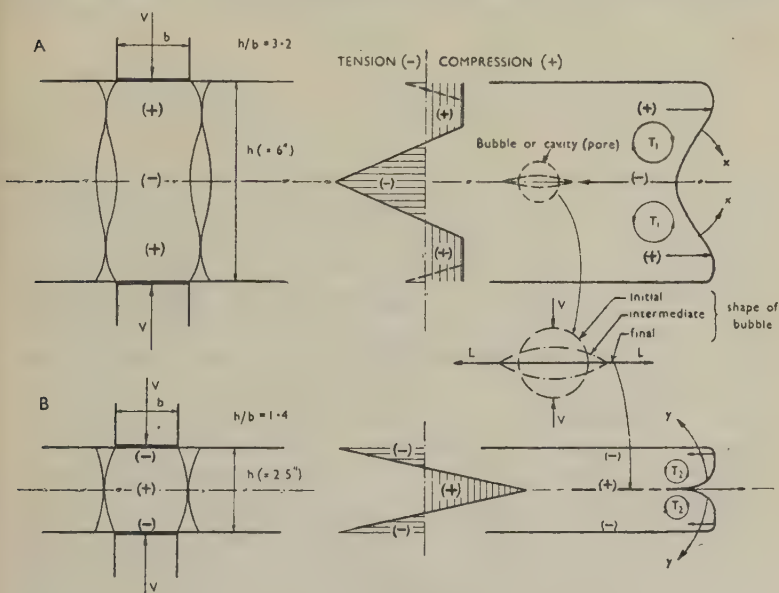


FIG. B. (Polakowski.)

chill-cast slabs such cracking was due exclusively to casting at too low a temperature or at too slow a speed; with continuous-cast slabs, tearing was usually due to stress cracks along the edge.

PROFESSOR H. O'NEILL,† D.Sc., M.Met., F.I.M. (Vice-President), referring to the paper by Kasz and Varley, said that he would like to underline for the benefit of students what the authors made clear in their paper, namely, that to them hot rolling was cold rolling in certain circumstances. In Fig. 8, (p. 420), for instance, they showed hardness contours in what, very roughly speaking, was hot-rolled metal, though in fact a good deal of cold rolling was taking place. Although the surface was harder than the centre in that figure, when the earlier stages of rolling were considered (p. 422), during which the metal was hotter and recrystallization took place, the surface of the metal was softer than the centre owing to that recrystallization.

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† Professor of Metallurgy, University College, Swansea.

At the top of p. 420 it had been stated that the top surface of the metal was more heavily worked than the bottom, and that the upper roll momentarily transmitted more power. Was there any case here for independent motors to drive the two rolls?

In the paper by Wilkinson and Fox the question of twinning in relation to deformation had been mentioned. In regard to the second paragraph on p. 475, was it fair to say that the authors there meant that deformation was facilitated by twinning? They said: "It is believed that, in addition to the inherent effect of the twinning itself, deformation is further facilitated by generation of new basal slip planes (0001) in the process". Yet on p. 477 they seemed to speak in the opposite sense when they said "... owing to resistance to deformation by twinning". Was there evidence that twinning produced an increased resistance to deformation?

DR. F. A. FOX,* F.I.M. (Member), said that, with regard to the point raised by Professor O'Neill, he was afraid it had not been made entirely clear in the paper that in the first case Mr. Wilkinson and he had been discussing twinning as probably one of the principal modes of plastic deformation in hot working, and in the second case (p. 477), twinning had been referred to in connection with the directionality of mechanical properties which resulted from the preferred orientation of the hexagonal lattice. In fact, in the hot-working process a great deal of twinning occurred. When certain crystals were stressed in such a direction as would favour any particular mode of deformation, those crystals would be deformed by that particular mode. It had also been said that the twinning process itself, when taking place after the exhaustion of basal and pyramidal slip would, by re-orientating the atoms in a particular crystal, produce new generations of basal planes on which slip could then take place by the normal mechanism.

As to the effect of twinning on the directionality of mechanical properties, at the bottom of p. 475 it was stated that "twinning is produced by tensile stresses in the direction of the hexagonal main axis and by compressive stresses at right angles to this axis". That was purely a crystallographic consideration, which was part of the nature of things and could not be altered, but it did result in a directionality of properties. For example, in a piece of thick plate, the prominent preferred orientation was one in which the hexagonal main axis was at right angles to the plane of the sheet, and since the twinning resulted in yielding at the lowest yield stress produced by tensile stresses in the direction of the hexagonal main axis and by compressive stresses at right angles to the axis, this meant that if it were possible to pull a tensile stress through the thickness of the sheet, the sheet would have a very low proof stress, because yielding by twinning in that direction would take place early. On the other hand, if a compression test through the thickness of the sheet were made, a high result would be obtained, because in the direction of the main hexagonal axis resistance to twinning by compression was at its greatest.

MR. C. E. DAVIES,† M.I.Mech.E. (Member), said he disagreed with Mr. Hessenberg in his suggestion that a larger roll diameter was to be preferred for rolling thick slabs. He noticed that in the test which had been carried out by Kasz and Varley in rolling samples of 12 in. wide slab reductions of something like 1 in. or more were taken; whereas in ordinary practice the reduction of such soft alloys as aluminium was only $\frac{1}{2}$ in. That did not seem to require necessarily a larger roll diameter, but greater pressure. The size of roll used in breaking down aluminium ingots was usually 34-40 in., and when there was an increase

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in the width of the slab and greater power was needed, a still bigger roll would be wanted—one which might become impossibly large from the practical point of view. That seemed to lead to the point of view that manufacturers would have to consider what was already practised in America, namely, the use of a 4-high mill for the earlier stages of breaking down heavy ingots.

In regard to the question of stagger, he was not sure whether the fact that the top layer of the slab moved more quickly than the lower layer was a serious matter from the metallurgical point of view, except that possibly it did encourage the crocodiling effect. The possibility that it might be due to the cooling of one side of the slab had not occurred to him before, and he had been inclined to think that it was entirely attributable to lubrication conditions, which were generally different on the top and bottom surfaces.

As to the friction hill, he assumed that Kasz and Varley were referring to the non-plastic areas. In cold rolling, particularly, the term friction hill was associated with that part of the load diagram in the roll gap which was caused by friction and which was triangular in shape in the diagram. He thought it might result in some confusion if the term were used in any other connection.

MR. I. D. TAVERNER,* B.E. (Member), referring to Mr. Smith's paper, said he thought there was another problem in extrusion, viz. the possibility of a variation in the physical dimensions of the extrusion. With the high-strength alloys that variation could be as much as 4 or 5% over the full length of the extrusion. Extrusions to-day were required, particularly by the aircraft industry, to extremely narrow limits. The problem of variation between the back and front of the billet was one which had to be solved, not only from the point of view of the metallurgical properties of the extrusion, but also from that of maintaining the dimensions uniform throughout the extrusion. The problem was, as would be expected, most acute with the high-strength alloys, where it was most important.

MR. N. D. G. MOUNTFORD † said the main difficulty with forged aircraft components was that they generally failed in fatigue, and from examination of those failures it was usually found that the fatigue cracks had originated in some minor defect or flaw. The designer realized that forgings could not in every case be expected to be entirely free from those minor defects. He therefore tried to place the defects in the position in which they could do least harm, and the forger provided him in most cases with facilities for doing this.

MR. F. E. STOKELD, ‡ F.I.M. (Member), referred to Fig. 8 (Plate LXII) of Mr. Smith's paper, which illustrated the author's contention that the difficulty of the development of large grain in heat-treated forgings might be overcome by giving the stock sufficient work in forging. He said he was glad that the author said "might" be overcome and added that this was not always practicable. To the user of extruded bars and billets for forging stock, the production of coarse peripheral grains was always a menace. If, however, it were only a matter of giving the stock sufficient work in forging, the forging industry should be able to deal with the matter to better effect than at present. Unfortunately, this was not the solution. Even on forging down to quite appreciable reductions, this coarse grain still remained.

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‡ Chief Metallurgist, The Deritend Stamping Co., Ltd., Birmingham.

MR. CHRISTOPHER SMITH,* F.I.M. (Member), recalled that, in introducing the papers, Dr. Smithells had said that he found it difficult to find a common factor that ran through them all. He himself thought that one could be traced, namely, the effect of friction. It occurred on both rolling and extrusion and now, in the production of large forgings, it was found to be the reason why Mr. Stokeld experienced difficulty in dissipating the large grain.

If a cylindrical billet were forged by means of a tool, intense friction arose along the faces in contact, so that when a certain amount of reduction had been effected, it was found that the original diameter of the specimen was retained, and that there were parts of the metal which, as in the case of the extrusion, completely escaped work. In the production of very large forgings, this effect was most pronounced, some areas being hardly worked at all while other areas were worked enormously, and were stretched out and refined locally. Thus there were great differences in uniformity in such forgings.

This led to the suggestion that the best alloys were perhaps not being used for the production of forgings. It might very well be that if the alloys were properly chosen, castings might give better service than some of the forgings which had been produced.

Commenting on the observations of Mr. Taverner in regard to dimensions of extrusion, Mr. Smith said that with the extremely high-speed extrusions referred to in his own paper, the dimensions were smaller than in the case of normal-speed extrusion. It seemed to him that the reason for the absence of speed cracks in these ultra-high-speed extrusions was that, in fact, the material was not coming in contact with the bearing of the die at all. He did not know why, and the point needed careful consideration, but it did appear that the production of ultra-high-speed extrusions free from these surface defects was due to the fact that friction was eliminated.

MR. R. B. SIMS † pointed out that Kasz and Varley in their paper, and Mr. Smith during the discussion, had drawn an incorrect analogy between the compression of a cylinder between rough parallel platens and the hot-rolling process. Although both were characterized by a high coefficient of friction between the tools and material, the velocity conditions during the deformation were essentially different. In the compression test, and in forging, the frictional shear stress between the material and the tools gave rise to a region at and below the surface where the plastic strains were small. In the hot-rolling process, it was known that the material near the surface of the billet was heavily worked, and this accounted for the distortion found by Kasz and Varley of the wires inserted vertically into ingots of aluminium, experiments which agreed well with Orowan's ‡ results from plasticine models.

During rolling, the material just outside the roll gap on the entry side and the unloaded material on the exit side might both be regarded as elastic, and would influence the deformation of the material between the rolls. If the arc of contact were long compared to the thickness of the strip, as in the majority of cases of cold rolling, the restraint due to this elastic material would be negligible, and the deformation might be regarded as homogeneous. In the rolling of ingots and slabs the length of arc of contact was often smaller than the ingoing thickness, and the inhomogeneous compression due to the restraint of the elastic material produced internal stresses leading to crocodiling and the variation in Brinell hardness shown in Fig. 8 (p. 420) of Kasz and Varley's paper. These strains had been measured in cold-rolled bearing

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† British Iron and Steel Research Association, Rolling Mill Research Laboratories, Sheffield University.

‡ E. Orowan, *Proc. Inst. Mech. Eng.*, 1943, 150, 140.

bronze by Baker, Ricksecker, and Baldwin,* and their results were applicable to hot rolling during the actual deformation, although stress relaxation might take place after rolling. From the work of Baker *et al.* it seemed that the ratio $\frac{\text{initial thickness}}{\text{length of arc of contact}} = \frac{H}{\sqrt{R\delta}} = \sqrt{\frac{H}{Rr}}$, where H = the initial thickness, R the roll radius, δ the draft, and r the fractional reduction, should be as small as possible, and one way to achieve this, as Kasz and Varley had indicated, was to make heavy reductions.

The explanation of edge cracking given on p. 424 was probably correct. Mican † had reached the same conclusion and linked the incidence of edge cracking with the ratios $\frac{\text{initial thickness}}{\text{length of arc of contact}}$ and $\frac{\text{width of billet}}{\text{initial thickness}}$. If the material was wide and thin, and was deformed between rolls of large diameter, the edges would bulge, and not form concavities, while the material increased in length with very little spread. Under these conditions the edges would be unsupported, and would be stretched during deformation giving rise to edge cracks.

MR. A. E. L. TATE, ‡ A.I.M., said he was not sure whether Wilkinson and Fox were right in saying that "... magnesium-zinc-zirconium alloys excel the others in hot workability. This is mainly consequent upon the high solidus, permitting the use of working temperatures of around 500° C., and the very fine grain-size of the cast stock," (p. 478).

He had found that if a binary 3% zinc alloy ingot was heat-treated for a long time (24 hr.) at about 320° C., it could be raised successfully to just below 500° C. and rolled, almost in the same way as the magnesium-zinc-zirconium alloys, and with a very coarse grain-size of the order of 50 times the size of the latter. Therefore, it seemed that the grain-size was not an important factor in the rollability of Z3Z.

DR. FOX said that he was familiar with Mr. Tate's work on the rolling of binary alloys, which showed that an alloy having a eutectic at about 340° C. could be solution-treated and then rolled at much higher temperatures. In the magnesium alloy containing 3% zinc, the solidus was raised to about 590° C. by the addition of zirconium, and generally speaking it could be said that very lengthy solution-treatment was rendered unnecessary. Rolling slabs were in practice given a short solution-treatment before rolling, but this was purely a safety measure designed to prevent any slight bleeding which might take place.

There was a considerable difference between the overall structure of a very large direct-chilled rolling slab, perhaps 40 × 15 × 5 in., and the structure of a much smaller chill-cast slab. In the latter there was a better chance of securing a uniform distribution of any second phase which might be present and therefore in the response to a solution-treatment. Even with direct casting, in the case of a very large slab, if zirconium were not present to inhibit the presence of a second phase, local areas were likely to be obtained which were so rich in the zinc-bearing phase that even a lengthy solution-treatment before rolling would not destroy the risk of cracking in the breaking-down operation.

On the question of grain-size, the scale effect was again a major factor. To break down a large slab was a very different matter from rolling quite a

* R. McC. Baker, R. E. Ricksecker, and W. M. Baldwin, Jr., *Trans. Amer. Inst. Min. Met. Eng.*, 1948, 175, 337.

† G. S. Mican, *Iron Steel Eng.*, 1949, 26, (2), 53.

‡ Metallurgy Division, National Physical Laboratory, Teddington.

small piece on small rolls. He knew that Mr. Tate had rolled a zirconium-containing alloy and found its rollability, as judged by the total absence of both edge cracking and surface cracking, to be comparable with that of the binary magnesium-zinc alloys. If, however, he had cast a binary alloy in a very large rolling slab and had attempted to break that down, even after prolonged solution-treatment, it was certain that he would have run into trouble, at least through local edge or surface cracking.

PROFESSOR A. J. MURPHY,* M.Sc., F.I.M. (Vice-President), said it seemed to him that not enough emphasis had been laid on the great advantages of effective grain refinement in ingots, particularly large ingots. It was not unnaturally the case sometimes that in making a large forging a sufficiently large ingot could not be employed to give the desired percentage reduction of section, and therefore a procedure was adopted which the manufacturer realized was not ideal, since he had not put as much work on the product as he would have liked. In those cases effective grain refinement with a cast ingot produced a markedly higher level of properties, and especially elongation, in the finished forging, as compared with a similar forging made with the same reduction of section with a coarser initial grain-size.

In the paper by Wilkinson and Fox passing reference was made to the magnesium-lithium alloys, but only to indicate that the discussion on plastic deformation given in the paper, which related to hexagonal structures, would not apply to those alloys. Some members might not have been aware that with 10% or more of lithium present in the magnesium alloys a body-centred cubic lattice existed which entirely changed the mode of deformation and the methods of working which could be used. Up to that time the history of magnesium alloys had been one of retardation through the difficulties inherent in the hexagonal close-packed lattice, which had had great economic consequences. It appeared, however, that if other economic difficulties arising from the price of lithium could be overcome, the magnesium-lithium alloys would open the way for the magnesium alloys to be shaped by methods and at speeds of working which hitherto had been applicable only to aluminium alloys among light alloys.

DR. W. M. DOYLE,† M.Eng., F.I.M. (Member), said that large numbers of high-strength light alloy forgings were sold to guaranteed figures in certain directions. When forgings and stampings were required for Class 1 applications, there should be and generally was a discussion between the customer and the manufacturer, at which an agreement was reached as to where the customer wanted the minimum properties, and in the past light alloy forgers had been very successful in providing those properties.

Dr. Doyle referred to the development of a technique for the manufacture of very large air-screw blades to D.T.D. specification No. 322, which, during the first two and a half years of the war, made possible the production of many thousands of such blades in the magnesium alloy Magnuminium 288A. With these large forgings, the cast dummies, about 250 lb. in weight, were gradually forged, the first operation being carried out on a 1000-ton press, the next stage being to swage the dummy in steps on a 3000-ton press, and the final pressing being carried out on a 5000-ton press.

MR. B. WALTERS,‡ M.A. (Member), said that in regard to the chill-cast stock mentioned by Wilkinson and Fox, he was not certain that soundness

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‡ Chief Metallurgist's Department, Imperial Smelting Corporation, Ltd., Avonmouth.

per se was so important, in view of the fact that the producers of steel ingots purposely made unsound ingots for rolling. He had found in work on magnesium rolling slabs that the important point was not to have the slab completely sound, but by choosing the casting method, especially with regard to the question of a fairly high degree of chill on the mould surface, to keep the unsoundness away from the surface of the slab. If the surface of the slab was sound and there was a good thick sound zone beneath, the slab would roll without very much cracking. On one small slab he had made, which was chill-cast at the base and the top of which was extremely porous, the base had been completely free from cracking and the top had cracked very badly.

DR. FOX referred to Fig. 11 (Plate LXIX) in the paper by Mr. Wilkinson and himself which showed an Elektron AM503 alloy rolling slab with a centre cavity. It had been found that central unsoundness disappeared with perfectly straightforward working up; but when dealing with alloys of a type which showed channelling forms of microporosity and even where this porosity was liable to occur without coming to the surface, one could not hope to get a reliable result if one started with a centrally unsound material. While he thought there was something in the point which Mr. Walters had made, he did not think that it was generally true. One would have to work with a sound ingot if threatened with the type of unsoundness liable to lead to internal oxidation.

MR. N. I. BOND-WILLIAMS,* B.Sc., A.I.M. (Member), said he wished to ask Mr. Smith why it was necessary to have a sharp edge to the extrusion-die orifice. In the first place, the extrusion die was used for more than one extrusion, and his experience with copper alloys was that after the die had been used once or twice, it was very difficult to maintain a sharp edge to the orifice, and in practice extrusion became easier as the sharp edge was worn away. Was the form of the die largely governed by the type of extrusion equipment available? Was it dictated by the production engineer, and would there be any advantage in using a die in which the flow was eased into the bearing rather than being abrupt? On looking at an extrusion discard, it could be seen that certain portions of the material had been stagnant, and those stagnant portions did in themselves form a lead into the die and might be regarded, once extrusion had started, as part of the die orifice itself.

On p. 447 Mr. Smith had said: "Many misguided attempts have been made to prevent the formation of the extrusion defect by varying the shape of the follower plate, by roughening its surface in contact with the back end of the billet, or by cutting grooves in its surface". His own experience, not on aluminium alloys but on brasses, had shown it to be possible to reduce the incidence of the extrusion defect by using a follower plate with a hemispherical (although not a full hemispherical) cavity, a fairly shallow depression, on the follower plate. This appeared to reduce the stagnant area at the top of the billet, and corresponded with the friction effect which other speakers had described where billets became stagnant in relation to the top or bottom dies of forging machines.

MR. CHRISTOPHER SMITH said he thought that the deciding factor in regard to the shape of the die was certainly the material being extruded through the die. The suggestion that the die shape had no bearing on the shape of the product was quite wrong. If an attempt were made to produce an extruded shape which was wide in relation to its thickness, using a die with a sharp edge and the same bearing all the way round, it would be found that the die

* Managing Director, Aston Chain and Hook Co., Ltd., Birmingham.

would not be completely filled because of the tendency of the metal to flow in the centre. In some techniques die-makers were able to induce the metal to flow to the extreme limits of the die by applying over an area on the die itself a quite generous radius of a type which affected the flow of the metal in the middle and forced it outwards. That was certainly true of aluminium alloy extrusion.

MR. R. E. BERRY,* M.Eng., A.I.M. (Member), referred to Figs. 1 and 2 of Smith's paper, stating that Fig. 1 showed a lead-in taper, whilst Fig. 2 did not. He asked whether this omission in Fig. 2 was intentional, and commented that if such a die was used for copper-base alloy extrusions the edges of the die would tend to turn inwards during the first extrusion and the back end would be, almost certainly, below size.

On the subject of cavities in followers, he stated that he had carried out some experiments to try to reduce pipe, and he could not agree with Mr. Bond-Williams that a shallow hemispherical cavity had any appreciable effect; it might reduce pipe by a few inches, but no more.

DR. J. W. JENKIN,† B.Sc., A.R.I.C., F.I.M. (Member), said that in the extrusion of steel the die shape was rather unlike anything previously mentioned. As Mr. Smith had rightly pointed out, the material being extruded had a profound effect.

AFTERNOON SESSION (Papers Nos. 1229-1232).

MR. G. L. BAILEY,‡ M.Sc., F.I.M. (Member of Council) (*Rapporteur*), in introducing the papers, said he would discuss the information given by each author on specific aspects of the hot-working process with a view to building up a general picture. For this purpose, he accepted the definition of hot working given by Cook and Davis in their paper (p. 501). Mr. Bailey then dealt with the mechanism of deformation; the scale of hot-working operations; factors affecting hot workability (including the effect of impurities); tests for hot workability; hot-working processes (rolling, extrusion, and rotary piercing); hot-working temperatures; and the effects of manufacturing conditions on the properties of the finished product.

DR. MAURICE COOK,§ F.I.M. (Member of Council), in connection with his definition of hot working, emphasized the need for a clear understanding that there was a real difference between the recrystallization temperature of a material which was in the cold-worked condition and in which recrystallization was effected by the subsequent application of heat, and what might be a possible recrystallization temperature in a material which was being deformed in the hot state.

MR. H. W. G. HIGNETT,|| B.Sc., F.R.I.C., F.I.M. (Member of Council), said that the authors of the papers in the Symposium were fortunate in dealing with materials whose hot-working properties were adversely affected only by minor constituents which were also undesirable from other points of

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|| Superintendent, Development and Research Department Laboratory, The Mond Nickel Co., Ltd., Birmingham.

view. In the case of nickel alloys, however, the service properties were often very much improved by minor additions which had a serious adverse effect on hot workability, and the problem of the economic commercial production of such alloys was frequently a matter of compromise. For this reason it was important to have available some method of assessing in the laboratory the probable behaviour of the materials in the hot-processing operations, when full-scale works' tests were not possible.

The first important factor to be considered in designing a satisfactory hot-working test was that of ingot structure. In his own laboratory they had therefore attempted to produce in small trial ingots the kind of structure which the alloy would have when cast in the works' ingot mould. A small-scale, square-section mould was used, on two faces of which cooling was deliberately retarded so as to displace the heat centre from the geometric centre. In fact, what was done was to use a graphite *L* in a large sand mould.

The second factor was the speed of deformation involved. In some of the alloys high rates of deformation produced work-hardening at temperatures far above the normal recrystallization temperature. One of the most useful tests consisted in cutting slices from the type of experimental ingot made in the special mould, heating these to selected temperatures, and compressing them across the corners by single blows from a drop hammer. The height of drop was adjusted to provide a reasonable degree of deformation for a given thickness of slice, and a speed of deformation correlating reasonably with the speed of deformation in the works' operation. This test had enabled the optimum range of temperature for forging experimental alloys to be selected and the effects of modifications in melting and refining technique to be compared. This test alone did not, however, permit the desired correlation of laboratory conditions with those of the works, and it had been found necessary to combine with it hot-bend tests of cast specimens and observations on the forging of samples very similar to those described by Cook and Davis. Hot tensile tests had proved quite valueless.

MR. HARRY DAVIES,* F.I.M. (Member of Council), said he thought the common factor in all the papers was the emphasis on the influence of grain-size on the structure of the casting. In working copper and copper alloys he had never observed that grain-size had very much effect, and he thought that in making a casting the primary objective should be soundness. In experiments he had carried out both on copper wire-bars cast in open moulds and on 70 : 30 brass, no variation of hot-working properties with grain-size had been observed, provided the castings were sound.

MR. E. J. BRADBURY,† M.Eng., A.M.I.Mech.E., A.I.M. (Member), said he would like to quote some data to amplify those given in Tables I and II (pp. 507, 508) of the paper by Cook and Davis and their remark that "The choice of initial working temperature and other conditions for fabricating an alloy on a manufacturing scale depends on both the metallurgical characteristics of the alloy, and the conditions most appropriate for the economic employment of the plant".

Table A gave the hot-rolling temperatures used for a series of nickel silvers on three different mills, and Table B the extrusion temperatures adopted for various nickel silvers.

He emphasized the importance of suitable hot-working tests, pointing out that now that the size of heats and the cost of materials and labour were so

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high, it had become increasingly important that the greatest yield of material should be obtained from a given heat.

TABLE A.—*Hot-Rolling Temperatures Employed in Three Different Mills for Nickel Silvers.*

Nickel Content, %	Rolling Temperature, ° C.		
	(a) Universal Mill	(b) Louth Mill	(c) Rod Mill
7	800	800	860–880
10	850	850	900–925
12	900	900	925–950
15	950	950	950
18	980	980	980
20	1000	1000	1000
25	1020	1020	1020
30	1050	1050	1050

TABLE B.—*Extrusion Temperatures for Various Nickel Silvers.*

Nickel Content, %	Extrusion Ratio	Temperature, ° C.	
7	—	800 *	
10	—	820 *	
12	—	840 *	
15	—	860 *	
18	—	800 *	
		Solid sections	Tube shells
20	22	900	900
—	18	880	880
—	16	860	880
—	14	850	880
—	12	850	860

* Average temperatures quoted for these compositions.

DR. MAURICE COOK said that the definition of hot working given by Davis and himself needed a little clarification. In the case of copper, the temperature at which recrystallization started was of the order of about 120° C., depending on the purity of the metal. It naturally varied with the composition and might exceed 300° C. with coppers containing certain amounts of silver. It should not be imagined from the definition given in the paper that, provided the metal was hot rolled at a temperature in excess of the recrystallization temperature, true hot rolling would result; it would not. On warm rolling copper at 300° or 400° C., very appreciable work-hardening effects occurred. Similarly, an ordinary α -brass hot rolled at 650° or 700° C. would substantially work-harden. The definition of hot rolling was intended to indicate that the material subsequently showed no appreciable evidences of cold working in the sense of a deformed crystal formation or appreciable hardening.

He disagreed with Mr. Davies in saying that the crystal structure of copper and copper-base alloys was not a matter of very much moment in hot working.

It was true that, in general, it might not be quite so important as it was with many aluminium alloys, but in copper, and in copper alloys especially, the crystal structure—not particularly grain-size as such, but the crystal configuration—of the ingot or the billet being processed was a matter of some consequence.

In aluminium brasses the crystal structure had a considerable influence, and in some cases of abnormal structure conditions, where the ingot consisted almost entirely of meeting systems of columnar crystals, cold rolling was virtually impossible and splitting resulted. To take another example in the hot-rolling field, as distinct from cold rolling, brasses of the 67 : 33 type were extraordinarily sensitive to crystal structure and configuration.

MR. A. LLOYD,* B.Sc., in discussing the paper by Back, said he agreed that most operations on lead and its common alloys fell into the category of hot working, even when carried out at room temperature, the chief exception being lead-tellurium alloy, where work-hardening took place and the hardness developed was retained for long periods.

While it was true that the fatigue properties of lead had been shown to be sensibly independent of grain-size, his experience was that at very slow rates of stress reversal grain-size played an important part, coarse-grained materials being least resistant.

With regard to lead pipe manufacture, the presses usually had a container capacity of about 7–10 cwt.; the use of small containers was confined to the extrusion of more difficult sections. He was in agreement with Back's conclusions regarding slug removal and the possibility of the formation of annular laminations in the product, though the difficulty could be minimized by an increase in the temperature and speed of the molten lead entering the container. If the temperature were high enough and the container were filled as quickly as possible, the residual slug would melt, at least on the top surface, and the oxide float to the top. Although bridge-core dies were regarded with suspicion in the lead industry, good-quality lead pipe could be made using these dies if careful attention was given to cleanliness of working. The temperature of extrusion was not so important as clean casting and freedom from lead oxide. Sound welds could be made by the extrusion of pre-cast billets, free from lead oxide, at comparatively low temperatures. The most important control factor other than composition was extrusion temperature, which had to be rigidly controlled to ensure a medium grain-size in the finished pipe. The importance of grain-size had rightly been emphasized by the author, as creep-resistance and freedom from intercrystalline cracking were dependent upon the retention of a medium and uniform grain-size in the pipe. Alloys containing small amounts of tin, antimony, or copper were the most difficult to control; initial fine grain-sizes were produced which recrystallized readily when strained at above 50° C., and hence non-uniform structures might result.

While it was true to say that pressures did not vary greatly under the normal conditions of extrusion of lead, differences resulted from the complexity of the shape being extruded, simple sections such as rod being easier to extrude than a long, narrow section having the same cross-sectional area.

In lead sheet manufacture, the castings mentioned by Back, 8 × 8 ft. × 6–8 in. thick, were the usual practice; these weighed some 10–12 tons each and called for care in lifting and handling at temperatures above 200° C., as the material was extremely soft.

In rolling 6–8% antimonial lead, experience suggested that it was essential

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to begin rolling at as high a temperature as possible consistent with safety, and to break down the brittle "as cast" structure as quickly as possible by a small number of heavy passes through the mill. After the initial break-down, rolling could be carried out at lower temperatures and in easier stages. Complete break-down of the original structure demanded a very high degree of reduction.

Lead sheet freshly rolled and on the mill bed in an unstrained condition had a fine and uniform structure which, however, was unstable, and when subject to strain behaved in one of two ways: (a) it might show grain growth and develop coarse structures, or (b) it might recrystallize entirely to form a new and stable structure. Lighter passes should be avoided in lead sheet rolling, as lead showed a tendency to retain very small amounts of cold work for periods up to 48 hr. The possible draft could be increased by the use of correct roll camber.

MR. A. V. GARNER,* M.Sc. (Member), said that the use of the extrusion process in both the cable and lead pipe industries was in some ways unique in that continuous lengths of tube were manufactured, which involved the welding together of several complete charges; another important difference from the hard-metal industry was that liquid charges were used in the container of the press.

Mr. Back had discussed some of the historical aspects of the development of the various types of presses and machines used in cable sheathing. The adoption of extrusion machines was, in theory, the complete answer to the problem of the split-lead defect, but these machines required careful manipulation if the dimensions of the tube and the rate of output were to be satisfactorily maintained.

In 1924, i.e. before extrusion machines appeared, the straight-through press was put into production, and this was the earliest successful attempt to modify the flow of lead in the container of the press to eliminate these radial weaknesses. The straight-through type of press made use of rather lower extrusion temperatures than either the extrusion machines or the vertical type of press, and so the difficulties of extruding 0.85% antimonial lead, which Mr. Back mentioned in his paper, did not arise to nearly the same degree.

Turning to a consideration of the effects of the hot-working process on the mechanical properties of the resulting cable sheath, Mr. Garner said that the work done during the last ten or twenty years at the British Non-Ferrous Metals Research Association and elsewhere had shown that the grain-size of lead and its alloys was particularly important in relation to their creep properties. Although it had been stated that the fatigue-resistance of lead was sensibly independent of grain-size, he agreed with Mr. Lloyd that it would be dangerous to generalize in the case of these alloys; the frequency and amplitude of the strain cycle should be considered, since it was reasonable to expect that a creep component would arise if the amplitude were sufficiently high and the frequency low. In fact, that type of strain was not uncommon in cable installations.

The grain-size could be controlled by a number of factors, such as alloy composition, extrusion temperature, and the rate of cooling from the extrusion temperature. The alloys normally used in cable sheathing had an inherently fine grain. Alloy "E", in particular, however, was more affected by the extrusion temperature and the degree of quenching in the die, than the antimonial lead alloys. In order to produce alloy "E" in a condition in which it would give its maximum creep-resistance, it was advantageous to work with

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a somewhat higher extrusion temperature in order to produce the medium grain-size to which Mr. Lloyd had referred in connection with lead pipes. Again, there was a parallel between the cable-sheath and lead-pipe industries in that cases had occurred where the structure of the tube proved to be zoned, as a result of coiling the tube while it was still hot and in such a condition as to cause intercrystalline cracking under creep conditions. This could be successfully avoided by quenching at the die.

Although this quenching might not be disadvantageous as regards the final mechanical properties of alloy "E", the possibility of age-hardening effects in the binary lead-antimony alloy could not be overlooked. Use had not yet been made of the age-hardening properties of these alloys as far as he knew. It was generally agreed that an age-hardening alloy would perform best under creep conditions if it were rendered metallurgically stable just above the temperature at which it was to operate in service. Some tests that he had carried out with fully heat-treated antimonial lead showed that a very marked change in creep properties occurred: whereas a normally extruded unquenched sheath would withstand a stress of 800 lb./in.² for, say, six months before breakdown, the same material fully heat-treated and aged would last appreciably more than twelve months. In this connection it had to be remembered that the inside of the cable could not be raised to very high temperatures, so that the required heat-treatment had to be applied at the die.

MR. R. CHADWICK said that on p. 575 of their paper Roberts and Walters stated that 0.02% iron could be tolerated without causing excessive cracking of zinc in hot rolling. That might be true of sheet rolling, but where zinc was to be rolled down to thin gauges in strip form, an iron content of this order could not be tolerated, and it would not be possible to make soft zinc strip for deep drawing with such material because the iron would completely prevent self-annealing, or, if sufficient heat were applied to cause softening, large grain growth would result.

On the same page, the authors stated that cadmium had a considerable solid solubility in zinc and led to work-hardening. They went on to say that "if a 'dead soft' sheet is required the cadmium content is limited to about 0.020%". That really depended upon what was meant by "dead soft". In his own work on zinc,* he had found that the addition of cadmium had a very considerable effect in accelerating self-annealing, and that whereas with a cadmium-free or substantially cadmium-free zinc a small amount of permanent cold work could be obtained, if any substantial amount of cadmium were added self-annealing inevitably occurred. It was true that when cadmium was added the zinc became somewhat harder, even in the annealed condition, and that might be what the authors intended to say; but it was not true, as they seemed to indicate, that cadmium additions permitted, or caused, the sheet to be hard in the sense that it did not anneal.

On p. 574, the authors referred to his own work on alloys containing magnesium, and stated that "the presence of 0.005-0.010% magnesium considerably increases the hardness and ultimate strength of cold-rolled zinc, the hardness increasing and the ultimate strength decreasing on subsequent ageing at room temperature". This statement appeared to result from an understandable misinterpretation of the data. The age-hardening of the zinc-magnesium alloys occurred so rapidly that a progressive change in the size of the diamond impressions during testing could be sometimes observed. In carrying out the tensile test, however, there was some slight delay before the specimen could be prepared and loaded into the testing

* *J. Inst. Metals*, 1933, 51, 93.

machine, and probably much of the initial age-hardening was by that time completed, so only the final re-softening process was detected.

In conclusion Mr. Chadwick referred to the paper by Showell on tin bronzes, saying that he thought the author had not brought out quite strongly enough the fact that the high-tin bronzes, with 20% tin, were extremely easy to hot work. A 20% tin alloy, within the right temperature range, namely 600°–700° C., was one of the easiest alloys to hot work, though it was unstable and had to be quenched immediately, as otherwise it became brittle. It was a very strong alloy when cooled and certainly seemed to him to be worthy of wider use than it had so far received.

M. VINAVER* said that bending capacity was an important mechanical property of zinc sheet, particularly in relation to its use for roofing, which was, in France, a major application. The anisotropy of zinc sheet, even after cross rolling was very marked. In this respect there was a great difference between sheet and strip, which was important in view of the present-day tendency in the case of all metals to employ strip rolling in place of the older processes. The strip obtained from ordinary zinc did not lend itself at all well to bending, so that the resultant product was unsuitable for roofing purposes. The difficulties were encountered when cadmium and iron were present together in amounts of the order of 0.01%.

An X-ray study of the textures of the surface and the interior of the strip revealed a marked difference: the basal plane at the surface was in the plane of the strip; in the deeper layers it was inclined at an angle of 20°. It appeared therefore that the anisotropy which resulted from the ordinary rolling as opposed to pack rolling had a possible effect on the bending capacity of zinc strip.

The application of modern strip-rolling methods was likely therefore to present greater difficulties in the case of zinc than in that of other metals, and M. Vinaver concluded by enquiring whether the production of ordinary zinc sheet by rolling as wide strip had yet been successfully attempted.

DR. D. E. R. HUGHES,† B.Sc. (Member), referred to the hot-torsion test as developed by the American workers Ihrig and Clark and Russ, mainly for steel, and mentioned by Cook and Davis in their paper (p. 510). The torsion test had the peculiar advantage that the rate of deformation stayed more or less constant from the start of the test to the end, whereas in a tensile or compression test, the rate of deformation altered because the dimensions of the test-piece changed. That was an advantage from the fundamental point of view of determining the mechanism of deformation at elevated temperatures. The torsion test had the further advantage that the amount of deformation that could be applied to the surface was very large.

MR. F. E. STOKELD said that Mr. Showell, on p. 536 of his paper, referred to the conditions required for hot working tin bronzes as opposed to cold working, and suggested that these "would not be satisfied by hot working, say, a bronze containing 10% tin and 0.1% phosphorus at 350° C.", adding that "It is probably this consideration that led to Stokeld's stating that only bronzes containing up to 2% tin and 0.1% phosphorus could be hot forged commercially".

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† Research Metallurgist, Tube Investments, Ltd., Birmingham.

His own words on this point in 1940 had had a rather different meaning from that now attributed to them. In the article quoted* he had been discussing the different copper alloys in which forgings and hot pressings were produced, and had written that true phosphor bronzes containing up to 1% phosphorus with 5% or 10% tin were very difficult to forge. He had added that most bronze forgings—implying phosphor bronze forgings—were made in forging-quality phosphor bronze which contained about 2% tin and up to 0.1% phosphorus. He would not like to say that, even to-day, only such a phosphor bronze—if it were a phosphor bronze—could be hot forged commercially. Chadwick's paper† showed that there were alloys with twice as much tin that exhibited reasonable to very good forging characteristics.

MR. R. E. BERRY asked whether the cylinders shown in Fig. 2 (Plate LXXII) of the paper by Cook and Davis were taken from the front or back end of extruded bars, and whether any difference had been found in the stamping qualities at the two ends.

The authors had mentioned that additions of iron and aluminium offset the embrittling effect of lead. Could they say something about the quantities involved to obtain that result, and had they also investigated other additions?

MR. EDWIN DAVIS,‡ M.Sc., F.I.M. (Member), replied that the samples shown in Fig. 2 had been taken from the centre of extruded bars. The difference in the hot-stamping quality of materials taken from front and back ends of extruded rod was not very marked, the front end being generally a little superior.

Improvement of the hot-working characteristics of leaded α/β brasses was brought about by the addition of 0.5–1% iron or 1.0–1.5% aluminium, depending to some extent on the amount of lead present. Such elements as tin, manganese, and nickel in similar amounts did not give rise to any improvement in the hot-working characteristics.

PROFESSOR A. J. MURPHY suggested, as an alternative to the definition given by Cook and Davis, that: "Hot working is the working of metals at temperatures at which progressive plastic deformation does not cause progressive increase in hardness".

He said that among the tin bronzes to which Mr. Showell referred, there was no mention of one which had a certain importance, viz.: the bronze with 1–7% tin containing iron and chromium in amounts of 1–2%. These tin bronzes were interesting because they were hot-workable and had been found to have very good properties as bearings. It was unusual to find a good bearing material which could be worked by forging, extrusion, and hot rolling.

MR. F. C. EVANS,§ (Member), said that the Symposium had reaffirmed his view that the extrusion process, while convenient from the production and engineering viewpoint, was still very unsatisfactory metallurgically. The paper by Smith on aluminium alloys, and that by Cook and Davis on copper and copper alloys showed that there tended to be a wide difference of properties and structure between the front and back ends of extruded rods. Up to the

* *Metal Ind. (Lond.)*, 1940, 56, 72.

† *J. Inst. Metals*, 1939, 64, 331.

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§ John Miles and Partners, Ltd., London.

present, this trouble still arose, in spite of much research, and it seemed from the data given in Smith's paper, that it was unlikely to be overcome, particularly in alloys with a high recrystallization temperature.

Rolling, on the other hand, had much to commend it for the production of bars and sections, as uniformity of structure from end to end was fairly easily obtained, owing to the equal amounts of work given to all sections of the bar, and to the relatively high speed at which the bar passed through the rolls, which ensured that there was little temperature difference between back and front. The latter point was of the utmost importance in dealing with alloys of complex structure, in which there were complicated phase changes in the region of the hot-working temperatures.

A representative alloy in this class was the nickel-iron-aluminium bronze of the nickel 5, iron 5, aluminium 10% type. On 2 in.-dia. bar extruded from a 6 in.-dia. billet weighing approximately 120 lb., a variation in 0.1% proof stress from 21 to 39.9 tons/in.² from front to back had been obtained. Other values, ranging from front to back, were :

U.T.S., tons/in. ²	48-54.3
Elongation, % on 2 in.	19-8.5
Brinell hardness no.	183-241

On smaller sizes of extruded bar even larger variations were to be expected. By rolling this alloy, on the other hand, it was relatively easy to obtain bars with extremely uniform properties and microstructure from end to end.

It might be argued that the extreme values quoted could be avoided by suitable cropping. It was nevertheless true that in this alloy the bar showed a progressive change in properties from one end to the other, as was only to be expected when it was remembered that the properties of the alloy depended largely on the form and amount of precipitated α , most of which was precipitated at or about the extrusion temperature.

Reference had been made earlier to the question of cropping extruded bar. The amount cropped off the front and back ends of the bar had, of course, an appreciable effect on the economics of the process. For example, to refer again to a specialized case, that of high-strength aluminium bronzes, the yield of good bar from finished billet was in the region of 75% or less for extrusion and 90% for rolled bar. As was shown in the Symposium * last year on ingot production, the yield of good cropped billet was approximately 80% for these alloys; it could therefore be calculated that the yield of good, finished, cropped bar from the weight of metal melted was approximately 60% for extrusion as against 72% for rolling.

Hence for the production of simple shapes in some alloys, rolling had considerable advantages over extrusion, both metallurgically and economically.

DR. MAURICE COOK replied that he thought it was fairly certain that the differences in properties cited by Mr. Evans were due to the extreme sensitiveness of the particular alloy cited to thermal treatments. The variation in properties between the front and back ends of brass rods was determined partly by extrusion conditions and also to a very large extent by the composition of the alloy. Even under relatively extreme conditions, however, the differences in properties between the front and back ends of extruded brasses—even those of the α/β type—were nothing like so marked as those quoted for the complex nickel-iron-aluminium bronze.

Had Mr. Evans taken any of the extruded bar from either the front or back end and heat-treated it? If so, did the heat-treatment result in a con-

* Symposium on Metallurgical Aspects of Non-Ferrous Metal Melting and Casting of Ingots for Working, *J. Inst. Metals*, 1948-49, 75.

siderable reduction of the difference in the properties of the bar in the extruded condition?

MR. EVANS replied that this had not been done. The figures quoted were all for bars as extruded and not for bars as heat-treated.

MR. W. T. BUTCHER* (Member), said it might easily be supposed that there were no problems associated with the rolling and extrusion of lead, but that was very far from being the case. One of the troubles arose from the large shallow type of melting pot traditional in the lead industry. It was commercially worth while to maintain a body of lead molten in a pot larger than that needed for immediate requirements just for the advantage of being able to keep it charged with overhead tackle, cranes, and so forth. There was therefore liable to be at any given time a large body of metal which was not immediately wanted and which was picking up oxide. That might have unfortunate consequences long afterwards in service.

MR. CHADWICK said that with reference to the question of zinc composition, he thought he could resolve the clash of opinion between Roberts and Walters and himself. At the bottom of p. 573 of their paper, it was stated: "It has been shown that the extent and permanence of the increased hardness obtained is influenced to a considerable extent by the amount of rolling, optimum properties being obtained at about 30% cold reduction". That was quite true if strength were required. Strength was needed in flat sheet, and the presence of 0.02% or even 0.05% iron was useful. The kind of zinc with which he himself had been mainly concerned was zinc strip in a dead soft condition for drawing, which was a very different matter, and in that case no more than 0.005% iron could be tolerated.

DR. A. LATIN,† M.Eng. (Member), said that a problem with which his firm was confronted arose in the extrusion of lead for cable sheathing required to withstand internal pressure, and was to eliminate the slow process leading to cracking of the extruded sheath in certain alloys with very small deformations under the internal pressure.

A factor in cable-sheath manufacture was the well-known charge-tongue effect. It was fairly certain that some of the charge-tongue troubles were due to oxide, and could be overcome by suitable precautions. But there was a point that was as yet ill-explained, namely, that in some antimonial alloys the charge-tongue itself suffered from brittleness under the slow creep or the slow fracture condition mentioned above, though in that case the effect was not always entirely due to oxide and such defects. There seemed to arise, as a result of the deformation in the extrusion process itself, some factor which afterwards caused an acceleration of ageing in the charge-tongue zone.

That was one of the types of problem requiring solution. Undoubtedly charge-tongue defects were due not only to the presence of impurities in between two charges, but also to differences in the temperatures concerned and the resistance to deformation of the two charges. It might be that in extrusion there was some effect of flow similar to a friction effect, causing a local disturbance in the material which afterwards left what amounted to internal stresses—possibly dislocation concentrations or something similar—which finally led to the accelerated change taking place.

MR. G. L. BAILEY, referring to Dr. Hughes's observations on the high-temperature torsion test for hot workability, said that the test had proved

* Research Manager, Goodlass Wall and Lead Industries, Ltd., Perivale, Middlesex.

† Research Department, British Insulated Callender's Cables, Ltd., London.

particularly suitable as a test of the hot-piercing characteristics of certain types of steel. However, tests of the high-temperature torsion behaviour of deoxidized copper with varying phosphorus contents were completely negative and showed no correlation at all with the rotary-piercing behaviour. Nor did any other type of test—high-temperature notch-bar impact tests, high temperature tensile tests, ordinary hot bend tests carried out at all sorts of speeds—give results bearing any relation to the capacity of those materials for rotary piercing.

CORRESPONDENCE.

MR. CLEMENT BLAZEY,* M.Sc. (Member): Although the excellent summary by Cook and Davis covers a great deal of ground, it leaves room for additional and confirmatory information on certain aspects of the subject.

First with regard to the hot rolling of cadmium copper. This alloy has a tendency to crack in the breaking-down passes, with cracking confined to only a proportion of the billets. In our experience at Port Kembla, we have found that cracking (i) is not due to the presence of metallic impurities; (ii) tends to vanish with the addition of phosphorus; (iii) is likely to occur, when present at all, in the two or more billets cast from a melt; (iv) is reduced in intensity, if not eliminated, by turning off the outer 0.25 in. or so of the billet (chemical analysis sometimes reveals an appreciably higher cadmium content in the outer than in the inner layers of a billet); and (v) is not appreciably affected by soaking the billets before rolling, varying the rolling temperature, or changing the shape and/or number of the breaking-down passes. The tendency to crack is inherent in the as-cast metal and would appear to have some connection with gas reactions, although the conclusion need not necessarily follow that cracking is proportional to the porosity of a billet.

Once over the breaking-down passes, the billets lose the tendency to crack unless—and this, of course, is exceptional—they contain lead. At odd times over a long period, small lots of billets have cracked badly through the accidental inclusion of lead in the foundry charge, possibly as a result of using a bundle of contaminated copper wire from cable-making operations. Lead at about 0.02% or more will cause cadmium copper to crack at all stages of hot rolling, even in the final coiling stage. This effect has been noticed in deoxidized as well as in oxygen-bearing billets. Lead cracking is therefore, distinguishable from what might be termed ordinary cracking.

Cook and Davis refer to the practice of imparting a degree of cold work to cadmium copper by pausing in the early stages of rolling. There is a possibility, however, that something more than mere cold working is involved in this practice. One can obtain a hard, high-strength rod by putting a billet straight through breaking-down and intermediate rolls and cooling the rod on the ramps between each pass in the finishing train, but this procedure may fail to produce a wire with as high a tensile strength as one floor-cooled at the breaking-down rolls. Apparently, the cooling has to be imparted at the right stage of rolling, which suggests that it may be due in part to a phase change, or may be the means of developing favourable fibre properties in the rod or wire. There is evidence on record that the tensile strength of hard-drawn copper wire varies from layer to layer because of changes in the degree of preferred orientation.

Experience at Port Kembla in the hot rolling of 2:1 brass shows that cracking occurs occasionally in the straight copper-zinc alloy containing only

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traces of lead. As Cook and Davis suggest, casting conditions and grain-size may be at the root of this trouble.

A matter not mentioned in the paper, but nevertheless of considerable interest, is the welding of blow-holes during hot working. It was raised, without eliciting a reply, by Mr. F. C. Evans * and by Dr. A. G. Ramsay † in the discussion on last year's Symposium on Metallurgical Properties of Non-Ferrous Metal Melting and Casting of Ingots for Working.

There is agreement among metallurgists that the gas-holes in H.C. copper wire-bars do weld in hot working. One line of proof can be furnished by turning a wire-bar to cylindrical shape, hot piercing it, cutting rings transversely from the shell, opening and flattening these rings, and then carrying out a torsion and reversed-torsion test on the square-section specimens so obtained. No sign of discontinuity will be seen on the opposed cut surfaces representing the inner part of the wire-bar. (This torsion test is superior to a tensile test for disclosing flattened blow-holes, as it covers a much greater surface of metal than a tensile fracture.) It is equally true, however, that the larger holes sometimes present in vertically cast phosphorus-deoxidized copper billets (both arsenical and non-arsenical) do not weld in either hot piercing or hot rolling, even though they reveal a clean surface as-cast or on being opened after hot working. As it is probable that a completely clean surface is not essential for the welding of copper (witness the occasional sticking or local welding of as-drawn coils of H.C. copper wire and deoxidized copper tubing in bright annealing), there would appear to be either a size factor involved or a gas present in the large holes that militates against welding.

With regard to the size factor, the following facts hold. In a copper billet of specific gravity 8.5 (a porosity of about 5% compared with hot-rolled or pierced metal, and comparable with that in a tough-pitch wire bar), the porosity could be obtained, theoretically, with one spherical hole of 0.45 in. dia. or 12,000 spherical holes of 0.02 in. dia., in each in.³; or, if a fiftieth of an inch is thought to be too small, with about 1500 holes of 0.04 in. dia. As the ratio of surface to volume is a function of diameter, the single large hole would have only about one-twelfth the surface area of the 1500 small holes. One would expect this difference to have some effect on weldability, but it would have to be considered in conjunction with the increase in surface area of each hole under the deformation imparted by hot rolling, piercing, or extruding. Dr. Ramsay's suggestion ‡ that the time required for diffusion of gas from cavity to metal might be a factor in welding, is worth attention in the light of this surface/volume relationship.

With regard to the nature of the gas, there is a possibility that large holes are not due to the same cause as small holes and are, therefore, filled with a gas of different composition, although their presence in conjunction with small holes (indeed, with holes of all sizes) suggests that they are due to gas release at solidification and not to the trapping of air or burning mould-dressing during pouring. The fact that, when porosity is present, all the billets of a crucible charge (for example, four billets each 3 in. in dia.) are likely to be more or less equally porous is also in favour of the view that the gas emanates from the charge as a whole. An abundance of small holes, probably filled with steam, often accompanies low phosphorus content (less than 0.01%), but holes of a wide range of size can be present with phosphorus of the order of 0.03%.

Then there is the possibility that, whereas small holes remain at grain boundaries, large holes form by accumulations of gas which create large

* *J. Inst. Metals*, 1948-49, 75, 1062 (discussion).

† *Ibid.*, 1091 (discussion).

‡ *Loc. cit.*

spaces with smooth retaining walls having no relationship to intergranular surfaces. However, the idea that intergranular surfaces might be disposed to weld readily is scarcely borne out by the observation of Evans * on the effect of hot work on phosphor bronze containing small holes.

The presence of phosphorus does not seem to be of direct importance, as phosphorus-deoxidized copper can be made to stick or weld locally by heating in hydrogen or in an atmosphere containing a proportion of hydrogen, e.g. one made from cracked ammonia. The possibility that the sticking of H.C. copper wire in bright annealing is associated with surface "gassing" through hydrogen embrittlement should not be overlooked.

That thoroughly porous H.C. copper billets made from partly compressed powder can be completely welded by extrusion in an atmosphere of steam with some hydrogen and/or carbon monoxide has been demonstrated by Stout † in his paper on the production of "sliverless copper rod".

It is obvious that experimental data are needed before definite conclusions can be drawn on the subject of welding of holes in hot working. An experimental study could conveniently be based on the effect of contact under static pressure of samples of different kinds of copper rod in different atmospheres over a wide range of temperature. Such a study, of course, would be an indirect means of approaching the gas-cavity or blow-hole aspect of the subject, but if the results were interpreted in the light of facts already determined on the sintering of copper powder and with due regard to the deductions of Phillips ‡ on the separation of gases from molten metals, they should be of considerable value.

DR. COOK and MR. DAVIS (*in reply*): In a paper of this type it is not possible to deal at length with the hot-working characteristics of all the alloys covered by the title, and Mr. Blazey's comments are a welcome contribution to the discussion. The cracking of cadmium copper in hot-rolling operations is not unusual and is, we believe, commonly associated with the presence of appreciable quantities of the cadmium-copper eutectic in the outer layers of the casting arising from inverse segregation. The tendency to cracking can be reduced by adopting conditions in melting and casting procedures which tend to minimize inverse segregation. Thus, effective deoxidation is helpful, as also is the provision of adequate chilling to promote rapid solidification. Our experience indicates that soaking the billets before hot rolling improves the hot-rolling characteristics, but if there is pronounced inverse segregation the soaking time necessary to give substantial improvement may be impractically long. The practice of completing the hot rolling of cadmium copper at relatively low temperatures in order to increase the strength of the final cold-drawn product is not unusual, and it would seem that the beneficial effect of this procedure is associated mainly with the development of a fine-grain structure rather than with a phase change.

As Mr. Blazey points out, whereas the numerous cavities present in tough-pitch copper ingots readily weld during hot working, those in deoxidized copper do not always do so and are a source of blisters or laminations in the wrought product. This difference in behaviour does not seem to be due to any inherent difference between the pressure-welding characteristics of the two materials, for recent work § || has established that both tough-pitch and deoxidized coppers readily pressure weld. The failure of blowholes in de-

* *Loc. cit.*

† H. H. Stout, *Trans. Amer. Inst. Min. Met. Eng.*, 1941, 143, 326.

‡ A. J. Phillips, *Trans. Amer. Inst. Min. Met. Eng.*, 1947, 171, 17.

§ M. Cook and E. Davis, *Trans. Inst. Weld.*, 1947, 10, 178.

|| E. Davis and E. Holmes, *J. Inst. Metals*, 1950, 77, (3), 185.

oxidized copper to weld during hot working would, therefore, seem to be associated with such factors as the size and distribution of the holes, their gas content and surface condition. If, as seems likely, it is necessary for any gas present to diffuse into the body of the metal before welding can take place then the size and number of the blowholes for any given degree of porosity are of importance in view of the surface/volume relationship to which Mr. Blazey draws attention, but information of the relative importance of all these factors is lacking.

DR.-ING. BERNHARD TRAUTMANN *: The usual German practice in the casting of zinc rolling slabs is somewhat different from that described in the paper by Roberts and Walters. In the production of slabs for pack rolling the moulds are filled by means of a ladle from a holding furnace. Continuous casting represents a possible future development. The mould temperature, which, in general, is about 150°C ., is somewhat higher than that given in the paper. Vertical moulds are not used to any great extent for casting unalloyed zinc. The slabs for pack rolling are not usually preheated, though slabs for the production of sheet for etching purposes are sometimes heated to 250°C . before rolling with the object of improving their homogeneity. The pre-heating temperature of between 140° and 200°C . quoted in the paper may be sufficient in the case of pure grades of zinc, but it appears rather low for the ordinary commercial grade. The account of the pack-rolling procedure employed in England shows that the slabs there are about twice as thick as those used in Germany. The number of sheets rolled in a pack, 15-30, is also higher than is usual in Germany.

As for strip rolling, commercial zinc high in lead is not generally strip rolled in Germany. The main reason for this lies in the considerable difficulties which are encountered in producing large slabs from commercial zinc. Open-type horizontal moulds cannot be used satisfactorily beyond a certain limit. Some other methods of casting which have recently been the subject of experiment, such as semi-continuous casting, have not been found entirely satisfactory. The disadvantages of vertical casting will be dealt with below.

It is reported in the paper that scalping before rolling exposes fine shrinkage cracks. The appearance of such cracks is certainly possible, but at the same time fine cracks which are noticeable after scalping are often due to milling or planing the slab surfaces. Columnar crystals which are formed at right angles to the surface of the slab and the hexagonal axes of which are perpendicular to the direction of growth, have a tendency to split along the basal planes when worked in the direction perpendicular to that of crystal growth. It has been shown particularly clearly in the case of single crystals, that the basal planes are also the planes of preferential cleavage. Such cracks are often confused with shrinkage cracks. Any machining of the surface of cast zinc slabs before rolling should therefore be avoided wherever possible, and if it is essential in some special cases to obtain a very clean surface machining should be preceded by a certain amount of hot working.

As for metallurgical considerations, cast zinc slabs consisting for the most part of unidirectionally oriented columnar crystals at right angles to the surface of the slab, possess, according to Edmunds, a fairly uniform structure over the whole cross-section. That is, their hexagonal axis is perpendicular to the direction of crystal growth, while their base is nearly parallel to it. During the rolling of such slabs some deformation can be obtained even with comparatively coarse columnar crystals, since the orientation of the basal planes favours slip. The reference to the figures for the tensile strength of columnar crystals parallel and perpendicular to the direction

* Cologne, Germany.

of crystal growth, as reported by Northcott, appears doubtful, since, owing to the basal slip, the strength is bound to be smaller in the direction of crystal growth than at right angles to it. The elongation values quoted make this clear.

The situation is appreciably more complicated in the case of vertical castings, where the directions of crystal growth vary. In semi-continuous castings, where the direction of crystal growth is mainly parallel to the longitudinal axis and where there are present in the outer zone only very small crystals perpendicular to the axis, differences of structure become apparent; for while the outer zone still yields comparatively easily to deformation by rolling, deformation in the interior is very small. Consequently, internal cracks appear during rolling and may extend right to the surface. For the same reason other methods of casting have also met with little success.

This crystal growth perpendicular to the surface is desirable for the rolling of zinc slabs and, at the same time, as fine a grain as possible should be aimed at. Such an arrangement provides the greatest capacity for slipping in zinc. Once the base has reached its final state basal slip is succeeded by twinning, which is encouraged by the rolling stress. Twinning can occur only if the rolling stress is able to shorten the *c*-axis, and this is possible only if the crystals are perpendicular to the surface, that is, parallel to the direction of the rolling pressure.

There are as yet few data available on the capacity of zinc for deformation, but the effect of certain impurities is beyond doubt. Burkhardt's statement that the maximum deformability of zinc containing 1% lead occurs at about 150° C. is subject to considerable modification in the presence of varying amounts of iron and tin and traces of certain other elements. Work still in progress tends to indicate that the resistance to deformation even of pure grades of zinc decreases at higher lead contents as the temperature is raised and particularly when it exceeds 150° C. It is noteworthy in this respect that the amount of work required to effect a given amount of deformation decreases very considerably at higher temperatures, and this fact may, in the case of very pure zinc, continue almost up to the melting point.

All the references available in the literature on the variation of the strength of zinc in relation to the rolling direction fail to take into account one of the most important factors, namely grain-size. The effect of the degree of rolling reduction should also be considered in this respect. Work carried out in Germany during the war, particularly on the subject of deep-drawing capacity, consistently showed the grain-size of the finished sheet to be a most important feature. Work still going on in Germany indicates that the relation of the tensile properties of the sheet to the direction is also greatly influenced by the grain-size. In this respect it should be emphasized that the orientation of the crystal axes in the cast slab is decisive in determining the grain-size of the finished sheet.

With regard to the influence of magnesium on zinc, it is worth noting that even contents as small as 0.005%, that is near the solubility limit, have a marked effect on the hardness and tensile strength, though the latter tends to diminish with prolonged storage.

It is stated in the paper (p. 574) that in horizontally cast slabs the orientation of the columnar crystals does not appear to be favourable to slip. This statement cannot be accepted unreservedly, as the formation of columnar crystals perpendicular to the surface of the slab is, in the case of an hexagonal lattice, comparatively favourable, at any rate more favourable than if the crystals were parallel to the surface. Naturally, the size of the columnar crystals has an important bearing on the deformability. All attempts to use the methods of continuous casting or of vertical casting have so far been fruitless, because it has not been possible to obtain a suitable columnar crystal

orientation in the interior of the slab. This also accounts for the considerable difficulties which have been experienced in breaking down the slabs, since after the preliminary passes the comparatively thin outer zone which is favourably oriented becomes rolled down to the maximum extent, and then cracks form inside the slabs which may in subsequent rolling penetrate to the surface.

The assumption that heavy cold working of zinc single crystals results in the formation of a preferred orientation of the basal plane, parallel to the slab surfaces, is not borne out by experiment. I have taken numerous X-ray photographs in order to see whether such a preferred orientation can be detected, but so far without success. Such an orientation could not be accounted for by the ordinary mechanism of deformation, since after slipping on the basal plane is complete twinning always occurs, and thus no preferred orientation could possibly be established.

MR. ROBERTS and MR. WALTERS (*in reply*): We wish to thank those who took part in the discussion of our paper and to reply to M. Vinaver's oral and Dr. Trautmann's written contribution.

With regard to the question at the end of M. Vinaver's remarks, it is stated in B.I.O.S. Report No. 1159, p. 79, that zinc strip 800 mm. wide was being rolled in Germany in 1945 and, presumably, still is. The rolling slabs were cast from a mixture of 50% G.O.B. zinc and 50% high-purity zinc which would probably result in a metal with a lead content of about 0.5%. It is understood also that the Montecatini Co. of Porto Marghera, Italy, are at present constructing a rolling mill designed to produce zinc strip of 1 m. width, but the grade of metal to be rolled is not known. No wide zinc strip is produced in Great Britain.

On the subject of directional bending properties of zinc strip, the opinion has been given* that providing the temperature at the breaking-down stage is carefully controlled the bending properties of strip zinc of fairly high purity, parallel and normal to the direction of rolling, would not show any marked differences.

We are very glad to have Dr. Trautmann's contribution, which has amplified a number of points considerably. His views appear to be substantially in agreement with those expressed in our paper. Though in connection with the statement in the penultimate paragraph that "All attempts to use the methods of continuous casting or of vertical casting have been fruitless", it may be remarked that in this country zinc rolling slabs are, in certain cases, cast quite successfully in vertical moulds.

* We are indebted to Mr. Holden, Manager of the Hall Street Metal Rolling Co., Ltd., Birmingham, for this information.

DISCUSSION ON THE PAPER BY DR. E. C. ELLWOOD AND MR. K. Q. BAGLEY: "THE STRUCTURE OF EUTECTICS."

(*J. Inst. Metals*, this vol., p. 631.)

DR. H. K. HARDY,* M.Sc., A.I.M. (Member): The authors have usefully added to our knowledge of eutectic alloys by confirming that an orientation relationship exists between the phases in some alloys. It would be of considerable interest to extend the work to suitable hypo-eutectic and ternary eutectic alloys. Cases may be imagined where the primary dendrites can determine the orientation of the eutectic colony, and where the orientation relationship between the phases in a ternary eutectic is exactly that of their binary eutectics, even though a continuous phase separates the other two phases in the ternary structure.

An orientation relationship is to be expected in many eutectics; their individual microstructures will, however, be controlled by the relative growth rates and volumes of the two phases. Surface-tension relationships will play a part in determining the equilibrium structure; this has been discussed in the paper by Thall and Chalmers.† The mode of eutectic crystallization will be described in correspondence on that paper.‡ Briefly, an orientation relationship may be anticipated where an easy matching plane exists in the lattices of the two phases. This enables a plane of atoms of the second component to be put down on the first-formed nuclei. The components will be deposited alternately to form a colony with a common orientation. If no easy matching plane exists, the two phases must nucleate independently from the melt and will then show no orientation relationship.

Dr. Ellwood and Mr. Bagley have raised, in their discussion, the general question of the existence of non-equilibrium conditions. The rate of change towards equilibrium is largely controlled by the rate of nucleation, and this is a function of the free-energy drop per atom of the new phase and the energy barrier due to the formation of the new interface.§ Once stable nuclei have been formed, the subsequent change towards equilibrium depends only on the rate of diffusion. Variation in the value of the authors' surface-energy factor, F_s , will affect the rate of nucleation by altering the height of the energy barrier. Thus, it is one of the factors controlling the degree of supersaturation which is required to enable a stable nucleus to be formed in a reasonable period of time. The effect of variation in the value of F_s on the position of the equilibrium phase boundary may be expected to be small, although the assumption of true equilibrium implies that the boundary interface between the two phases is a plane.

It is difficult to follow the reasoning which leads the authors to their equation:

$$\Delta F = -\Delta F_m + \Delta F_s$$

* Head of Physical Metallurgy Section, Fulmer Research Institute, Ltd., Stoke Poges, Bucks.

† B. M. Thall and B. Chalmers, *J. Inst. Metals*, 1950, **77**, (1), 79.

‡ H. K. Hardy, discussion on above paper, to be published in *J. Inst. Metals*.

§ H. K. Hardy, *J. Inst. Metals*, 1950, **77**, (5), 457.

which they take to represent the free-energy change, ΔF , when an alloy "which is in equilibrium under a given set of conditions is treated in such a way as to disturb the equilibrium". ΔF_m is here the change in the "chemical factor" and ΔF_s the change in the surface-energy factor. There is no *prima facie* reason why these terms on the right-hand side of the equation must necessarily have opposite signs. Similarly, as long as the requirements tacitly present in the authors' argument are fulfilled, i.e. that they are dealing with a given alloy at a given temperature, I am unable to subscribe to the view that conditions can be altered from equilibrium without changing ΔF from zero, or that ΔF must necessarily remain zero when conditions are altered. If ΔF were to remain zero, the alloy would always be in an equilibrium condition, i.e. a state of lowest energy. Under this hypothesis, there would be no possibility of an overall drop in free energy to provide the driving force for reactions such as spheroidization, on annealing.

The authors mention one corollary of their hypothesis, that the solid solubility would depend on the particle-size of the second phase and decrease as the particle-size is decreased. A second corollary is that the solubility should decrease as the quantity of the second phase of equal particle-size is increased.

As the authors' equation is not acceptable, it is necessary to examine the variation of free energy and to determine the change in solubility with a decrease in particle-size. Both these factors may be obtained from the derivation of the Thomson-Freundlich formula for the vapour pressure of curved surfaces as given by Glasstone.*

It is assumed that the solutions are ideal, so that Raoult's law is obeyed and vapour pressure is proportional to the concentration. Let x_0 be the concentration of the solution in contact with a flat surface of the second phase, and x_1 be the concentration of the solution in contact with a convex particle of radius r . If dm/M moles of the solute be transferred from the plane solid to the particle, the increase in free energy of the solution is:

$$\Delta F_{\text{soln.}} = \frac{dm}{M} RT \ln \frac{x_1}{x_0}$$

where M is the molecular weight of the solute. Suppose that the addition of dm g. of the component increases the surface of the particle by da , the increase in free energy of the particle is:

$$\Delta F_{\text{particle}} = \sigma da,$$

where σ is the interfacial free energy. The total change in the free energy of the system is the sum of these two positive terms:

$$\Delta F_{\text{system}} = \Delta F_{\text{soln.}} + \Delta F_{\text{particle}}$$

For the particle and solution to be in equilibrium their free energies per g.-molecule must have been increased equally so that:

$$\Delta F_{\text{soln.}} = \Delta F_{\text{particle}}$$

$$\text{Putting } a = 4\pi r^2, da = 8\pi r dr, m = \frac{4}{3}\pi r^3 \rho, dm = 4\pi r^2 \rho dr$$

where a is the area of the spherical particle, r is its radius, m is its mass, ρ is the density, and dr is the increase in radius accompanying the increase in area da , we get:

$$da = \frac{2dm}{r\rho}.$$

* S. Glasstone, "Textbook of Physical Chemistry", 2nd edn., p. 495. New York: 1946 (D. Van Nostrand Co.); London (Macmillan and Co., Ltd.).

Hence :
$$\Delta F = \sigma da = \frac{2\sigma dm}{r\rho}$$

from which :
$$\ln \frac{x_1}{x_0} = \frac{2\sigma}{r} \frac{M}{\rho} \frac{1}{RT}$$

$$= \frac{2\sigma}{r} \frac{V}{RT}$$

where V is the gramme molecular volume.

Thus a decrease in particle-size of the second phase is to be associated with an increase in free energy and with an increase in the solubility limit, in contradiction to the authors' hypothesis. The change in solubility will, however, normally be inappreciable until the radius becomes very small.

Variations of solubility with grain-size have been reported for aluminium-copper alloys by Phillips and Brick,* as mentioned by the authors. Wiest † and Dehlinger and Wiest ‡ have reported similar effects in copper-silver alloys, although the effect has been denied by Schmid and Siebel.§ Even if such a variation in solubility with grain-size were completely proved, it would not be relevant to the authors' hypothesis. A variation of solubility with grain-size may be accounted for by a different concentration at the crystal boundaries compared with that within the grains. This would arise from the requirements of the Gibbs adsorption theorem,|| which makes the surface (or interfacial) concentration dependent on the relative surface (or interfacial) energies of the solute and solvent. Solute atoms which lower the interfacial energy of the crystal boundaries would be expected to concentrate in these regions and vice versa. Dean and Davey ¶ have used this to account for the lower copper content of the grain boundaries in zinc-copper alloys, and the subject has also been examined by Benedicks.**

Nothing is known with certainty of any variation of solid solubility with variation in the boundary area of coexisting phases. If any effects are observed, the Gibbs adsorption theorem represents a more promising starting point for their explanation than the Thomson-Freundlich formula.

The AUTHORS (*in reply*) : We thank Dr. Hardy for his remarks and agree that it would be of interest to extend the work to other types of alloy structure in which two or more phases appear simultaneously. However, we do not contemplate any such investigation in the near future, although some aspects of eutectic solidification are being studied in our department at King's College, Newcastle, at present. We agree that such simple orientation relationships as have been found are not universal, and we believe that the aluminium-silicon eutectic is a case in point.

Dr. Hardy has stressed the importance of the nucleation of one phase by another during eutectic solidification, but we have not attempted to discuss this factor because we think that insufficient factual evidence is available to allow the principles involved to be clearly understood. Some of the principles are under investigation by another worker in the Department of Metallurgy, and, while we do not wish to anticipate his findings, the present indications

* A. M. Phillips and R. M. Brick, *Metallwirtschaft*, 1933, 12, 161; *J. Franklin Inst.*, 1933, 215, 557.

† P. Wiest, *Z. Physik*, 1932, 74, 225.

‡ U. Dehlinger and P. Wiest, *Metallwirtschaft*, 1933, 12, 2.

§ E. Schmid and G. Siebel, *Metallwirtschaft*, 1932, 11, 685.

|| F. H. Newman and V. H. L. Searle, "The General Properties of Matter", 4th edn., p. 148. London : 1948 (Edward Arnold and Co.).

¶ G. R. Dean and W. P. Davey, *Trans. Amer. Soc. Metals*, 1938, 26, 267.

** C. Benedicks, *Kolloid Z.*, 1940, 91, 217.

are that the problem may be slightly more complicated than Dr. Hardy has suggested.

With regard to the effect of surface area, our contention is that the free energy of the system is made up of two terms $F_m + F_s$, which we have called the chemical and surface energy respectively, and that these energies may be altered, but not independently, without altering the total free energy of the system. It was not intended to imply that the free energy was at a minimum, since strictly this could only be the case when the surface-energy term was very small, as it might be if the phase present in least amount existed as a single spherical particle. For complete treatment on a mathematical basis the concentration of each component in each phase, as well as the interfacial energy effect, should be taken into consideration. This is not the case with the Thomson-Freundlich equation.

Dr. Hardy's proposition requires a close examination. His preliminary steps leading to the equation :

$$\Delta F_{\text{system}} = \Delta F_{\text{soln.}} + \Delta F_{\text{particle}}$$

we think to be incorrect, perhaps as a result of over-refinement. There is no reason, mathematical or otherwise, to believe that the transfer of solute from a plane to a small particle is accompanied by an increase in free energy of the solution. The solution in equilibrium with the particle, if affected at all, could only have its concentration diminished as the particle increased in size, leading, we suggest, to a reduction in free energy of the solution; but the equation concerned takes no account of such a change.

The first conclusion from the mathematical illustration we regard as rather ambiguous. If it is deduced from the expression :

$$\Delta F = \frac{2\sigma dm}{r\rho}$$

that the free energy of a particle increases as the particle-size decreases, this would appear to be in direct contradiction to the original statement that :

$$\Delta F_{\text{particle}} = \sigma da,$$

where the free energy associated with the surface clearly increases with increase in surface area.

ΔF is not dependent upon $\frac{1}{r}$, as the equation above seems to indicate, but upon $\frac{dm}{r}$, i.e. $\frac{r^2 dr}{r}$, and is therefore proportional to $r dr$. Thus the energy of the particle decreases as the radius is reduced, which is to be expected; but $\frac{\Delta F}{dm}$, the energy per unit mass, increases as the particle-size decreases, which is in accord with our hypothesis. We agree, however, that the solubility of particles, at least of a pure phase, should increase with decrease in particle-size, from a consideration of the Thomson-Freundlich relationship. This leads to a higher free energy, which is not consistent with our view that the total free energy may remain constant throughout.

Although the variation of solid solubility with grain-size is not strictly relevant to our discussion of possible changes in solid solubility resulting from variation in inter-phase contact area, it was introduced as indicating that area of intergranular contact (compared with inter-phase contact in our case) appears to affect solid solubility.

FURTHER DISCUSSION ON THE PAPER BY DR. H. K. HARDY : " MODERN DESCRIPTIVE THEORIES OF PRECIPITATION PROCESSES."

(*J. Inst. Metals*, 1948-49, **75**, 707, 1160.)

DR. H. M. MEYER* : Dr. Finlay adds a note to Dr. Hardy's stimulating review that " recently, it has been shown that aluminium-zinc alloys show a very marked reversion ". An earlier experiment, however, was performed in the late Dr. W. H. Fraenkel's laboratory.

Dr. Hardy, incidentally, defines reversion as " the loss of hardness or other properties produced by a very short heating above the ageing temperature and subsequent re-ageing at the lower temperature ". It is, therefore, perhaps worth putting on record that, while Dr. Gayler discovered the loss of hardness produced by heating,† the original " subsequent re-ageing at the lower temperature " after a very short heating, which was to give reversion its name, was first observed in an aluminium-zinc alloy.‡

The AUTHOR (*in reply*) : I would like to thank Dr. Meyer for his interesting comments. He is quite correct in drawing attention to the important contributions to our knowledge of age-hardening phenomena which we owe to W. Fraenkel and his co-workers. A few papers from Dr. Fraenkel's laboratory which describe the effect of successive ageing treatments at different temperatures are listed below.§ These date from approximately the same period as Dr. Meyer's work and the subject is still being studied and discussed.||

* Newark, N.J., U.S.A.

† M. L. V. Gayler, *J. Inst. Metals*, 1922, **28**, 233.

‡ H. Meyer, *Z. Physik*, 1932, **76**, 268.

§ W. Fraenkel and L. Marx, *Z. Metallkunde*, 1929, **21**, 2. W. Fraenkel, *ibid.*, 1930, **22**, 84; 1931, **23**, 172.

|| H. K. Hardy, *J. Inst. Metals*, 1950, **77**, (5), 457.

DISCUSSION ON PAPER BY PROFESSOR A. KRUPKOWSKI AND MR. S. KAWINSKI: "THE PHENOMENON OF ANISOTROPY IN ANNEALED POLYCRYSTALLINE METALS."

(*J. Inst. Metals*, 1948-49, **75**, 869.)

IR. J. H. PALM * (Member): In this paper the authors suggest that the degree of anisotropy in sheet or plate metal can be fully evaluated from the tensile test on a specimen in the direction of rolling only. However, for a complete picture of the anisotropy, especially with regard to the x and y directions (Fig. A), tensile tests in the x as well as the y direction are necessary.

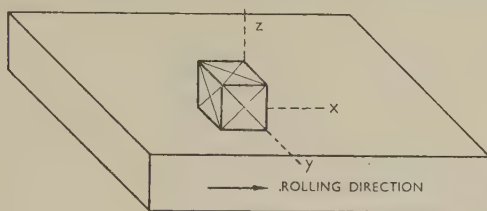


FIG. A.

As elucidated in a recent paper,† in the general case of triaxial loading, each of the strains in the principal directions consists of two partial strains.

Using true strains, instead of conventional strains as is done by the authors, we have :

$$\begin{aligned}\eta_x &= \eta_{xy} + \eta_{xz} \\ \eta_y &= \eta_{yx} + \eta_{yz} \\ \text{and} \quad \eta_z &= \eta_{zx} + \eta_{zy}\end{aligned}$$

whilst $\eta_x + \eta_y + \eta_z = 0$, since the volume may be regarded as constant.

For the uni-axial tensile test in the x direction, $\eta_{yz} = \eta_{zy} = 0$; hence $\eta_{yx} = \eta_y$ and $\eta_{zx} = \eta_z$; whilst for the tensile test in the y direction $\eta_{xz} = \eta_{zx} = 0$, and hence $\eta_{xy} = \eta_x$ and $\eta_{zy} = \eta_z$. The tensile test in the x direction therefore yields directly the relations between the stress and the partial strains η_{xy} and

η_{xz} , and hence the coefficient of anisotropy $K_{yz} = \frac{\eta_{xy}}{\eta_{xz}}$. From the test in the

y direction we obtain the relations between the stress and the partial strains η_{yz} and η_{yx} and hence $K_{zx} = \frac{\eta_{yz}}{\eta_{yx}}$.

* Head, Materials Department, Nationaal Luchtvaartlaboratorium, Amsterdam, Holland.

† J. H. Palm, *Appl. Sci. Research*, 1949, [A], **2**, (1), 54.

It now seems reasonable to assume that at least for annealed anisotropic metals the relations between the partial strains γ_{xy} , γ_{yz} , and γ_{zx} and the stress are identical to the relations between the partial strains γ_{yx} , γ_{zy} , and γ_{xz} and the stress.

We then have :

$$K_{xy} = \frac{\gamma_{zx}}{\gamma_{zy}} = \frac{\gamma_{xz}}{\gamma_{yz}},$$

so that K_{xy} can also be obtained from the tests in the x and y directions. A test in the z direction, which is almost impracticable, is then superfluous. At equal stresses in the separate tensile tests we then also have :

$$K_{xy} \cdot K_{yz} \cdot K_{zx} = \frac{\gamma_{zx}}{\gamma_{yz}} \cdot \frac{\gamma_{xy}}{\gamma_{xz}} \cdot \frac{\gamma_{yz}}{\gamma_{xy}} = 1.$$

Since, as the authors have shown, one of the coefficients is independent of the stress, the same will apply for the other coefficients, so that the product of the three coefficients of anisotropy is equal to 1, irrespective of the stresses at which they are determined.

It is obvious that, contrary to the authors' suggestion, K_{yz} gives incomplete information on the anisotropy. In fact K_{xy} is of more significance for the evaluation of the anisotropy of sheet metal than is K_{yz} or K_{zx} . However, a complete picture is only given by the relations between the stress and the three partial strains (partial stress-strain curves) separately.

Editor's Note : No reply to the above contribution has been forthcoming from the authors.

OBITUARY.

HORACE WADSWORTH GILLETT.

Dr. H. W. Gillett, former director of Battelle Memorial Institute, died from a heart attack on 3 March 1950 near Nicholasville, Ky., while on his way home from a hunting trip in Florida and Georgia.

Horace Wadsworth Gillett was born in Steuben County, N.Y., on 12 December 1883 and attended Cornell University, receiving his A.B. degree in chemistry in 1906. After graduation, he taught physical and electrochemistry at Cornell while working for his doctorate degree. During summer vacations, he worked as a chemist with Thomas A. Edison and with Arthur D. Little, Inc. He was awarded the Ph.D. degree in 1910, and in the same year was made manager of the research department of the Aluminum Castings Company, Detroit.

In 1912 he became associated with the U.S. Bureau of Mines as an alloy chemist, and later became chief alloy chemist in charge of the field station in Ithaca, N.Y. Twelve years later he succeeded George K. Burgess as chief of the Division of Metallurgy, U.S. Bureau of Standards.

By 1929 Dr. Gillett had become recognized as one of the outstanding metallurgists in the United States, and was chosen by the board of trustees of the Battelle endowment to direct the newly founded Battelle Memorial Institute. He selected the staff of scientists and initiated the plan of operation which was responsible for the development of Battelle into the largest endowed research foundation in the United States. In the same year he accepted the responsibility of the editorial direction of the monthly magazine *Metals and Alloys* (now *Materials and Methods*), publication of which was then just beginning.

A scientist rather than an administrator by inclination, Dr. Gillett resigned from his directorship of Battelle in 1934, and from then until early in 1949, he acted as chief technical advisor, in which position he was responsible for the technical guidance of the Institute's research. As chief technical executive, he passed every technical report and research paper that left the Institute, and it is generally conceded that the success Battelle has obtained results largely from the high standard of technical excellence upon which he insisted. At the time of his death Dr. Gillett was serving as technical consultant to Battelle.

In addition to his Battelle duties, Dr. Gillett found time for extensive writing (he was a master of the "correlated abstract") and participation in the research activities of professional societies. He was a member of the American Institute of Mining and Metallurgical Engineers, the American Society for Metals, the American Society for Testing Materials, the American Foundrymen's Society, the American Chemical Society, the Electrochemical Society, the Iron and Steel Institute, and the Institute of Metals, which he joined in 1910. His professional honours included: McFadden Gold Medallist (American Foundrymen's Association), Henry Marion Howe Memorial Lecturer (American Institute of Mining and Metallurgical Engineers), and Edward Williams Lecturer (Institute of British Foundrymen). He served on several committees of the American Society for Testing Materials.

During the recent war, Dr. Gillett served on the Advisory Committee on

Metals and Minerals to the U.S. War Production Board and as a member of the Research Division of the War Metallurgy Committee.

Outside his professional field, Dr. Gillett was known throughout the United States as a keen sportsman and dog lover. He was affiliated with the Columbus Bird Dog Club and was interested in hunting, fishing, sailing, and skeet shooting.

ROOSEVELT GRIFFITHS.

The death occurred at Swansea on 24 June 1950 of Mr. Roosevelt Griffiths, Lecturer in Metallurgy at the University College of Swansea.

Mr. Griffiths was born on 13 May 1903, attended Pontypridd Secondary School, and entered the University College of Swansea in 1922, graduating B.Sc. in 1925. After a short period on the staff of Robert Gordon's College, Aberdeen, he returned to Swansea as a research assistant in 1926. In 1927 he was appointed assistant lecturer, and in 1930 lecturer on the permanent staff of the College, a position which he held until his death. He was awarded the degree of M.Sc. in 1930 for a thesis on "The Oxidation of Steel with Special Reference to Blistering of the Oxide". His continued interest in this subject resulted in the award of Carnegie Scholarships in 1936 and 1938. His publications include papers on oxide formation in the *Journal of the Iron and Steel Institute* and a text-book "Thermostats and Temperature Measuring Instruments".

He took a considerable interest in local and national metallurgical societies, and was especially active in reviving interest in the South Wales Local Section of the Institute of Metals after the 1939-1945 war. In addition to holding office in this Section between 1931 and 1939, he was an ordinary Member of Council of the Institute from 1940 to 1945, and a Vice-President from 1945 to 1948, serving on the Membership, Meetings, Local Sections, and Future Policy Committees. He was also a member of the Iron and Steel Institute, a founder Fellow and Member of Council of the Institution of Metallurgists, and President of the Swansea and District Metallurgical Society for the session 1949-1950. He joined the Institute in 1930.

D. W. HOPKINS.

ROBERT JAMES McLEOD.

Mr. R. J. McLeod, Chairman and Managing Director of the Power Plant Co., Ltd., West Drayton, Middlesex, died on 27 December 1949.

Robert James McLeod was born at West Hartlepool in 1882, and served his apprenticeship with Messrs. Richardson, Westgarth and Co. Afterwards, in 1903, he went to sea as an engineer, becoming a chief engineer with the Furness Line. Ten years later Mr. McLeod forsook the sea in order to become general manager of the Steam Fittings Co., Ltd., and while he was with that firm he designed and patented a number of special valves, steam traps, &c.

In 1918 he joined the board of the Power Plant Co., Ltd., as managing director, in which position he continued until his death. For the last ten years he had also been chairman of the company. Mr. McLeod's chief interest lay in the improvement and development of gear-cutting processes and plant, and he was the sole patentee of the "Finroc" process of gear shaving. He was a founder member and Past-President of the British Gear Manufacturers' Association.

Mr. McLeod joined the Institute of Metals in 1917.

NAME INDEX.

- Allen, N. P.** Discussion on "The Mechanism of Deformation in Metals, with Special Reference to Creep", 731.
- Andrews, K. W.** Discussion on "Recrystallization of Single Crystals After Plastic Bending", 672; discussion on "The Application of X-Ray Methods to the Determination of Phase Boundaries in Metallurgical Equilibrium Diagrams", 689.
- Appleton, Ronald John Walter.** Elected member, xx.
- Arnold, Brian.** Elected student member, xvii.
- Asbury, Frederick Ernest.** Elected student member, xviii.
- Aston, Charles Frederick.** Elected member, xv.
- Austin, Peter.** Elected student member, xxi.
- Ayala, Urbano Lopez.** Elected member, xiv.
- Aziz, Mostafa Kamal Abdel.** Elected student member, xxi.
- Back, L. H.** Paper: "The Hot Working of Lead and Lead-Rich Alloys", 541.
- Bagley, K. Q.** See Ellwood, E. C.
- Bailey, G. L.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 764, 773; elected Member of Council, xxiii; proposes vote of thanks to retiring President, xxiii.
- Bailey, Harold John.** Elected member, xv.
- Bailey, William.** Elected member, xiv.
- Baker, W. A.** Discussion on "Modern Billet Casting, with Special Reference to the Solidification Process", 662.
- Banks, Clarence Kenneth.** Elected member, xvii.
- Bannister, William Joseph.** Elected member, xv.
- Barnes, Sidney Mellish.** Elected member, xviii.
- Bartnik, George.** Elected student member, xvii.
- Becker, Jean.** Elected student member, xx.
- Bell, Henry B.** Elected student member, xvii.
- Bell, Raymond Charles.** Elected member, xvi.
- Berry, Brian Shepherd.** Elected student member, xvii.
- Berry, R. E.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 764, 771.
- Beton, Robin Hartley.** Elected student member, xvii.
- Bhat, Uppinangady Gopalkrishna.** Elected student member, xv.
- Biggs, Derek Leonard.** Elected student member, xxi.
- Biggs, William Derrick.** Elected student member, xviii.
- Bilby, B. A.** Paper: "Static Models of Dislocations", 613.
- Binney, Humphrey Lockhart.** Elected member, xx.
- Blazey, Clement.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 774.
- Bond-Williams, N. I.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 763.
- Botham, George Henry.** Elected member, xv.
- Bourne, Alan Arthur.** Elected student member, xviii.
- Brace, A. W.** Discussion on "Grain Refinement of Aluminium and Its Alloys by Small Additions of Other Elements"; "The Mechanism of Grain Refinement of Sand Castings in Aluminium Alloys"; "The Effect of Grain-Size on the Tensile Properties of High-Strength Cast Aluminium Alloys", 745.
- Bradbury, E. J.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 765.
- Bradley, Donald.** Elected student member, xv.
- Brenner, P.** Discussion on "Modern Billet Casting, with Special Reference to the Solidification Process", 663.
- Brown, A. F.** Discussion on "Recrystallization of Single Crystals After Plastic Bending", 673.
- Butcher, W. T.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 773.
- Butler, Edmund Marshall.** Elected member, xiv.
- Cahn, R. W.** Paper: "Recrystallization of Single Crystals After Plastic Bending", 121; reply to discussion, 675.

- Campbell, C. S.** Discussion on "Grain Refinement of Aluminium and Its Alloys by Small Additions of Other Elements"; "The Mechanism of Grain Refinement of Sand Castings in Aluminium Alloys"; "The Effect of Grain-Size on the Tensile Properties of High-Strength Cast Aluminium Alloys", 747.
- Cantrell, J.** Discussion on "The Application of X-Ray Methods to the Determination of Phase Boundaries in Metallurgical Equilibrium Diagrams", 697.
- Carlile, S. J., and W. Hume-Rothery.** Paper: "A Note on the Effect of Nitrogen on the Structures of Certain Alloys of Chromium and Manganese, and on the Existence of an Intermediate Nitride Phase", 195; reply to discussion, 719, 722.
- **J. W. Christian, and W. Hume-Rothery.** Paper: "The Equilibrium Diagram of the System Chromium-Manganese", 169.
- Carlsson, Carl Georg.** Elected member, xix.
- Carmina, Rosario.** Elected member, xx.
- Cartmell, Leo John.** Elected student member, xxi.
- Catling, Jack Harold.** Elected member, xvi.
- Chadwick, R.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 752, 769, 773.
- Chandaria, Devchand P.** Elected member, xix.
- Chatterjee, Ajit Kumar.** Elected student member, xvii.
- Chatterjee, Asit Kumar.** Elected student member, xviii.
- Chaudhuri, Arup Ratan.** Elected student member, xx.
- Chaudron, Georges.** Autumn Lecture: "Recent French Investigations in the Field of Light Alloys", 1.
- Chilton, John Pollock.** Elected student member, xviii.
- Christian, J. W.** Discussion on "The Application of X-Ray Methods to the Determination of Phase Boundaries in Metallurgical Equilibrium Diagrams", 692; *see also* Carlile, S. J.,
- Cibula, A.** Paper: "The Mechanism of Grain Refinement of Sand Castings in Aluminium Alloys", 321; remarks at opening of discussion, 744; reply to discussion, 748.
- and **R. W. Ruddle.** Paper: "The Effect of Grain-Size on the Tensile Properties of High-Strength Cast Aluminium Alloys", 361; remarks at opening of discussion, 744; reply to discussion, 748.
- Clarebrough, L. M.** Discussion on "Grain Refinement of Aluminium and Its Alloys by Small Additions of Other Elements"; "The Mechanism of Grain Refinement of Sand Castings in Aluminium Alloys"; "The Effect of Grain-Size on the Tensile Properties of High-Strength Cast Aluminium Alloys", 747.
- Clogenson, Georges Henry Jean.** Elected member, xiv.
- Conder, Peter.** Elected student member, xxi.
- Congreve, Walter Kendall.** Elected student member, xvii.
- Cook, Maurice, and Edwin Davis.** Paper: "The Hot Working of Copper and Copper Alloys", 501; reply to discussion, 764, 766, 771, 772, 776.
- Cooper, Norman.** Elected student member, xx.
- Crowther, J.** Paper: "Overheating Phenomena in Aluminium-Copper-Magnesium-Silicon Alloys of the Duralumin Type", 201; reply to discussion, 728.
- Crowther, John Raymond.** Elected student member, xxi.
- Cupp, Calvin Robert.** Elected student member, xvi.
- Cutler, Percy.** Elected member, xvi.
- Davies, Brian Gowan.** Elected student member, xx.
- Davies, C. E.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 758.
- Davies, Colin James.** Elected student member, xviii.
- Davies, George.** Elected member, xiv.
- Davies, Harry.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 765; elected Member of Council, xxiii.
- Davies, Roy Bartlett.** Elected member, xiv.
- Davis, Edwin.** *See* Cook, Maurice.
- Davis, Richard John.** Elected student member, xviii.
- Dennis, Thomas John.** Elected student member, xx.
- Dickens, Arthur.** Elected member, xvi.
- Donaldson, John William.** Elected student member, xxi.
- Dovey, D. M., and I. Jenkins.** Paper: "The Behaviour of Nickel-Chromium-

- Iron Alloys in Carbon-Bearing Gases in the Range 900°–1000° C.**, 581.
- Dowding, Michael Frederick.** Elected member, xviii.
- Doyle, W. M.** Discussion on "Modern Billet Casting, with Special Reference to the Solidification Process", 664; discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 762.
- Dutta, Sudhendu Kumar.** Elected member, xvi.
- Eborall, Myriam D.** Paper: "Grain Refinement of Aluminium and Its Alloys by Small Additions of Other Elements", 295; reply to discussion, 748.
- Elkington, Ronald William.** Elected student member, xxi.
- Elliott, Eric.** Elected member, xvi.
- Elliott, Ronald.** Elected student member, xviii.
- Elliott, Sam John Lloyd.** Elected student member, xv.
- Ellwood, E. C., and K. Q. Bagley.** Paper: "The Structure of Eutectics", 631; reply to discussion, 782.
- El-Mehairy, Ahmed Ezzat.** Elected student member, xvi.
- Evans, Brian.** Elected student member, xviii.
- Evans, F. C.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 771, 773.
- Ewen, Ian Elrick.** Elected member, xx.
- Faulkner, Charles Raymond.** Elected student member, xx.
- Féron, André.** Elected member, xiv.
- Finch, Donald Ira.** Elected member, xiv.
- Fleming, Graham.** Elected student member, xxi.
- Fodor, Gabriel.** Elected member, xviii.
- Fowler, W. A.** Awarded W. H. A. Robertson Medal, xxiii.
- Fox, F. A.** See Wilkinson, R. G.
- Franklin, William Walter.** Elected member, xiv.
- Fransès, Claude.** Elected student member, xv.
- Gardam, G. E.** Discussion on "Some Aspects of the Production and Heat-Treatment of Electrolytic Copper Powder", 659.
- Gardner, Robert Nathan Henry.** Elected member, xix.
- Garner, A. V.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 768.
- Gayler, M. L. V.** Discussion on "The Mechanism of Deformation in Metals, with Special Reference to Creep", 732; discussion on "Grain Refinement of Aluminium and Its Alloys by Small Additions of Other Elements"; "The Mechanism of Grain Refinement of Sand Castings in Aluminium Alloys"; "The Effect of Grain-Size on the Tensile Properties of High-Strength Cast Aluminium Alloys", 747.
- Gillett, Horace Wadsworth.** Obituary notice, 787.
- Glaisher, W. H.** Paper: "A Method of Improving the Pressure-Tightness of Lead-Free Gun-Metal Sand Castings", 377.
- von Goldbeck, (Frl.) Ortrud.** See Kubaschewski, O.
- Goldschmidt, H. J.** Discussion on "The Application of X-Ray Methods to the Determination of Phase Boundaries in Metallurgical Equilibrium Diagrams", 693.
- Goodlad, Wilfred Horace.** Elected member, xiv.
- Goodwin, Harold.** Elected member, xix.
- Graham, A.** Discussion on "The Mechanism of Deformation in Metals, with Special Reference to Creep", 733.
- Green, Terence Edwin.** Elected student member, xvii.
- Greenfield, Peter.** Elected student member, xvi.
- Gregg, John Fleming.** Elected student member, xviii.
- Griffiths, Roosevelt.** Obituary notice, 788.
- Grimston, John.** Elected member, xiv.
- Hägg, Gunnar.** Elected member, xv.
- Hall, John Richard.** Elected student member, xxi.
- Hampton, Donald.** Elected student member, xviii.
- Harbord, Reginald John.** Elected student member, xxi.
- Hardy, H. K.** Discussion on "A Note on the Effect of Nitrogen on the Structures of Certain Alloys of Chromium and Manganese, and on the Existence of an Intermediate Nitride Phase", 718; discussion on "The Structure of Eutectics", 780; reply to discussion on "Modern Descriptive Theories of Precipitation Processes", 784; *see also* Sully, A. H.

- Harris, Derek William.** Elected student member, xxi.
- Harris, Louis Reuben.** Elected student member, xvii.
- Harris, Solomon Wilfred.** Elected student member, xx.
- Hawkins, Neville.** Elected student member, xvii.
- Hawley, William H., Jr.** Elected student member, xxi.
- Heal, T. J.** *See* Sully, A. H.
- Hentz, Åke G.** Elected member, xix.
- Herne, Howard James Louis.** Elected member, xviii.
- Heslop, John.** Elected student member, xviii.
- Hessenberg, W. C. F.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 754.
- Hignett, H. W. G.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 764.
- Holt, Martin Oswald.** Elected student member, xxi.
- Holth, Tore.** Elected member, xviii.
- Honeycombe, R. W. K.** Discussion on "Recrystallization of Single Crystals After Plastic Bending", 673; discussion on "The Mechanism of Deformation in Metals, with Special Reference to Creep", 734.
- Houseman, David Henry.** Elected student member, xvii.
- Hudson, Robert Frederick.** Elected student member, xviii.
- Hughes, Charles Robert William.** Elected member, xix.
- Hughes, D. E. R.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 770.
- Hugo, Jacques Pierre.** Elected student member, xvii.
- Hume-Rothery, W.** Discussion on "The Application of X-Ray Methods to the Determination of Phase Boundaries in Metallurgical Equilibrium Diagrams", 679; *see also* Carlile, S. J.
- Jackson, Horace Ernest.** Elected member, xvi.
- Jackson, William James.** Elected student member, xx.
- Jamieson, Archibald.** Elected student member, xvii.
- Jenkin, J. W.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 764.
- Jenkins, I.** *See* Dovey, D. M.
- Jessop, Alan Fields.** Elected student member, xviii.
- Johannsson, Thor.** Elected student member, xviii.
- Jones, E. H.** Elected Member of Council, xxiii.
- Jones, W. R. D.** Discussion on "The Application of X-Ray Methods to the Determination of Phase Boundaries in Metallurgical Equilibrium Diagrams", 697.
- Jordan, Michael Frederic.** Elected student member, xvi.
- Josephs, Ellis.** Elected member, xiv.
- Kalling, Bo Michael Sture.** Elected member, xix.
- Kasz, F., and P. C. Varley.** Paper: "The Hot Rolling of Aluminium and Its Alloys", 407; reply to discussion, 754, 755, 757.
- Kawinski, S.** *See* Krupkowski, A.
- Kay, Gerald Harry.** Elected student member, xvii.
- Keen, (Miss) Maureen Sheila Marie.** Elected student member, xvii.
- King, Ronald.** Elected member, xix.
- Koenig, Hans M.** Elected student member, xvii.
- Kondic, V.** Discussion on "Modern Billet Casting, with Special Reference to the Solidification Process", 665; discussion on "Grain Refinement of Aluminium and Its Alloys by Small Additions of Other Elements"; "The Mechanism of Grain Refinement of Sand Castings in Aluminium Alloys"; "The Effect of Grain-Size on the Tensile Properties of High-Strength Cast Aluminium Alloys", 747.
- Krupkowski, A., and S. Kawinski.** "The Phenomenon of Anisotropy in Annealed Polycrystalline Metals" (correspondence), 785.
- Kubaschewski, O., and (Fr.) Ortrud von Goldbeck.** Paper: "On the Mechanism of Oxidation of Nickel-Platinum Alloys", 255; reply to discussion, 740.
- Kula, Eric Bertil.** Elected student member, xx.
- Kuo, Ke-hsin.** Elected student member, xx.
- Laker, William Eric.** Elected student member, xxi.
- Lamouredieu, Marcel.** Elected member, xix.
- Latin, A.** Discussion on "The Mechanism of Deformation in Metals, with Special Reference to Creep", 736;

- discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 773.
- Lauriente, Mike.** Elected student member, xvii.
- Lázló, Franz Michael.** Elected member, xx.
- Lea, Albert Dennis.** Elected student member, xvii.
- Lewis, William Edmund Jenkin.** Elected member, xiv.
- Liander, Nils Halvard.** Elected member, xix.
- Lindh, Erik Gunnar.** Elected member, xx.
- Lissell, Erik Olof.** Elected member, xix.
- Lloyd, A.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 767.
- Lloyd, Raymond Charles.** Elected student member, xx.
- Lord, James Osborn.** Elected member, xix.
- McConnell, Alex McDonald.** Elected member, xxi.
- Macdonald, William Richardson Dicksor.** Elected member, xiv.
- Mackay, James Matthew.** Elected student member, xxi.
- McLeod, Robert James.** Obituary notice, 788.
- Mantle, Edward Charles.** Elected member, xix.
- Maréchal, Jean.** Elected member, xv.
- Marshall, J. B.** Elected student member, xx.
- Mehta, Surendra Raj.** Elected student member, xxi.
- Mercer, Randolph.** Elected member, xviii.
- Meredith, George.** Elected member, xv.
- Meyer, H. M.** Discussion on "Modern Descriptive Theories of Precipitation Processes", 784.
- Michael, Anthony Dennis.** Elected student member, xxi.
- Milko, John Anthony.** Elected member, xiv.
- Millward, Humphrey John.** Elected member, xviii.
- Mincher, A. L.** See Ruddle, R. W.
- Mitchell, Gordon H.** Elected student member, xvii.
- Mocarski, Stanislaw.** Elected member, xix.
- Modin, Sten Olof.** Elected member, xix.
- Moffatt, Robert Sydney Martin.** Elected student member, xvi.
- Moir, Douglas Newlands.** Elected student member, xxii.
- Molinder, Anders Göran.** Elected member, xix.
- Mondolfo, L. F.** Discussion on "Overheating Phenomena in Aluminium-Copper-Magnesium-Silicon Alloys of the Duralumin Type", 726.
- Morris, D. P.** See Owen, E. A.
- Morrison, John Lamb Murray.** Elected member, xvi.
- Morton, James Storrs.** Elected member, xiv.
- Mountford, N. D. G.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 759.
- Munnick, Eric Howard.** Elected member, xiv.
- Murphy, A. J.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 762, 771; elected Senior Vice-President, 1950-51, xxiii; seconds vote of thanks to retiring President, xxiv.
- de Nardo, Juan Bautista.** Elected member, xix.
- Needleman, Benjamin.** Elected member, xv.
- Newman, W. A. C.** Presents Hon. Treasurer's Report, xxii.
- Newton, James Welsby.** Elected member, xvi.
- Nicholls, Christopher.** Elected member, xxi.
- Nisbett, Edward George.** Elected student member, xvii.
- Noden, Joseph Desmond.** Elected student member, xviii.
- Norén, Tore M. I.** Elected member, xxi.
- Nygren, Erik.** Elected student member, xx.
- Olds, Geoffrey Charles Edward.** Elected student member, xviii.
- Olt, Theodore F.** Elected member, xix.
- O'Neill, H.** Discussion on "Recrystallization of Single Crystals After Plastic Bending", 675; discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 757; elected Vice-President, xxiii.
- Owen, E. A., and D. P. Morris.** Paper: "The Application of X-Ray Methods to the Determination of Phase Boundaries in Metallurgical Equilibrium Diagrams", 145; remarks at opening of discussion, 677; reply to discussion, 698.

- Padley-Smith, Arthur Edwin.** Elected member, xv.
- Paish, Ralph.** Elected member, xvi.
- Palm, J. H.** Discussion on "The Phenomenon of Anisotropy in Annealed Polycrystalline Metals", 785.
- Palmer, Arthur Robert.** Elected student member, xxii.
- Pandurangiah, Vummidi.** Elected member, xxi.
- Pearson, W. K. J.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 754.
- Pell, Frederick Roy.** Elected student member, xxii.
- Pfeil, L. B.** Elected Member of Council, xxiii.
- Pile, Bryan Harold.** Elected student member, xxii.
- Place, Arthur.** Elected member, xv.
- Polakowski, N. H.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 755.
- Pomeroy, Patrick Reginald Dan.** Elected student member, xvii.
- Pontremoli, Pio.** Elected member, xxi.
- Poole, David Michael.** Elected student member, xvii.
- Porter, John Moser.** Elected student member, xxii.
- Portevin, Albert.** Awarded Institute of Metals Medal, xxv.
- Potter, Pat.** Elected student member, xxii.
- Primus, Francis Charles.** Elected member, xvi.
- Rachinger, W. A.** See Wood, W. A.
- Rathenau, Gerhart W.** Elected member, xviii.
- Raven, Richard Tebbitt.** Elected member, xix.
- Raynor, G. V.** Discussion on "The Application of X-Ray Methods to the Determination of Phase Boundaries in Metallurgical Equilibrium Diagrams", 685; elected Member of Council, xxiii.
- and **R. A. Smith.** Paper: "The Constitution of the Silver-Rich Silver-Magnesium-Zinc Alloys", 389.
- Reitsema, R.** Elected member, xviii.
- Ricksecker, Ralph E.** Elected member, xvi.
- Roberts, C. W., and B. Walters.** Paper: "The Rolling of Zinc and Zinc-Rich Alloys", 557; reply to discussion, 779.
- Roca Soler, José.** Elected member, xv.
- Rogers, T. Howard.** Paper: "A Method for Assessing the Relative Corrosion Behaviour of Different Sea-Waters", 597; elected member, xv.
- Rooksby, H. P.** Discussion on "The Application of X-Ray Methods to the Determination of Phase Boundaries in Metallurgical Equilibrium Diagrams", 696.
- Ruddle, R. W.** See Cibula, A.
- and **A. L. Mincher.** Paper: "The Thermal Properties and Chilling Power of Some Non-Metallic Mould Materials", 43.
- Russell, John.** Elected member, xviii.
- Rybczynski, Ludwik.** Elected member, xvi.
- Ryder, Colin David.** Elected student member, xvi.
- Ryder, Dennis Arthur.** Elected student member, xvii.
- Samuel, Philip.** Elected student member, xix.
- Samuels, L. E.** Paper: "The Metallography of Copper Containing Small Amounts of Bismuth", 91; reply to discussion, 660.
- Schaub, Cyril.** Elected member, xix.
- Scheuer, E.** Paper: "Modern Billet Casting, with Special Reference to the Solidification Process", 103; remarks on opening of discussion, 662; reply to discussion, 669.
- Schramm, Jacob.** Elected member, xv.
- Schrero, Morris.** Elected member, xxi.
- Scutts, William.** Elected student member, xvii.
- Sergeant, William John Clive.** Elected member, xvi.
- Shakespeare, William George.** Elected student member, xx.
- Sharp, Herbert John.** Elected member, xvi.
- Sharp, Peter Edward.** Elected student member, xvi.
- Shelvington, William Edwin.** Elected member, xvi.
- Showell, D. W. Dugard.** Paper: "The Hot Working of Tin Bronzes", 527.
- Siddiqi, Rafiq Ahmad.** Elected member, xxi.
- Sims, R. B.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 760.
- Smallman, Raymond Edward.** Elected student member, xx.
- Smith, Christopher.** Paper: "The Extrusion of Aluminium Alloys", 429; reply to discussion, 763; discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 760.

- Smith, Cyril Stanley.** Discussion on "Overheating Phenomena in Aluminium-Copper-Magnesium-Silicon Alloys of the Duralumin Type", 726; discussion on "The Aluminium-Tin Phase Diagram and the Characteristics of Aluminium Alloys Containing Tin as an Alloying Element", 742.
- Smith, Eugene Monroe.** Elected member, xvi.
- Smith, James Arthur.** Elected member, xv.
- Smith, R. A.** See Raynor, G. V.
- Smithells, C. J.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 752.
- Smout, (Sir) Arthur.** Moves alteration to provisions of Clause 3 of Memorandum of Association, xiii; announces foundation of Walter Rosenhain Medal, xxii; moves adoption of Report of Council, xxii.
- Speirs, Archibald.** Elected student member, xvii.
- Spiegelberg, Arne Per Wilhelm.** Elected member, xix.
- Spray, Charles Alan Francis Thomas.** Elected student member, xxii.
- Stevens, John Rupert.** Elected member, xix.
- Stewart, Maxwell Hector.** Elected member, xix.
- Stokeld, F. E.** Paper: "The Hot Forging and Hot Stamping of Aluminium and Its Alloys", 453; discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 759, 770.
- Strong, Geoffrey Victor.** Elected student member, xxii.
- Sully, A. H.** Discussion on "A Note on the Effect of Nitrogen on the Structures of Certain Alloys of Chromium and Manganese, and on the Existence of an Intermediate Nitride Phase", 719.
- **H. K. Hardy and T. J. Heal.** Paper: "The Aluminium-Tin Phase Diagram and the Characteristics of Aluminium Alloys Containing Tin as an Alloying Element", 269; reply to discussion, 743.
- Swan, J. C.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 757.
- Swanson, Colin John.** Elected student member, xx.
- Tasker, H. S.** Elected President, 1950-51, xxiii.
- Tate, A. E. L.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 761.
- Taverner, I. D.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 759.
- Taylor, Alan Frederick.** Elected student member, xx.
- Taylor, Henry George.** Elected member, xv.
- Taylor, Robert Clive.** Elected member, xv.
- Terry, Robert Brian.** Elected student member, xvii.
- Thexton, J.** Discussion on "Modern Billet Casting, with Special Reference to the Solidification Process", 666.
- Thomas, Donald E.** Discussion on "On the Mechanism of Oxidation of Nickel-Platinum Alloys", 738.
- Thomas, W. J.** Awarded W. H. A. Robertson Medal, xxiii.
- Thompson, F. C.** Elected Vice-President, xxiii.
- Thompson, Lawrence S.** Elected member, xvi.
- Timmis, Laurence Barnett.** Elected member, xv.
- Trautmann, Bernhard.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 777.
- Trehearne, Edward Brian Geoffrey.** Elected student member, xxii.
- Tuchschmid, Eugen Heinrich.** Elected member, xvii.
- Tucker, Herbert Toyne.** Elected member, xxi.
- Tyrrell, H. J. V.** Paper: "Some Aspects of the Production and Heat-Treatment of Electrolytic Copper Powder", 17; reply to discussion, 659.
- Van Lancker, Marc.** Elected member, xv.
- Varley, P. C.** See Kasz, F.
- Vaughan, Charles Stanley.** Elected student member, xx.
- Vinaver, —.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 770.
- Waine, Fred.** Elected member, xviii.
- Wainhouse, Donovan Michael.** Elected student member, xix.
- Wakeling, Albert Lorraine.** Elected member, xv.
- Wallace, Eben Richard.** Elected member, xix.

- Walters, B.** Discussion on "Metallurgical Aspects of the Hot Working of Non-Ferrous Metals and Alloys", 762; *see also* Roberts, C. W.
- Waters, Brian Harry Coles.** Elected student member, xv.
- Watkins, Harry Clifford.** Elected member, xix.
- Whitfield, John France.** Elected member, xx.
- Whitwham, Donald.** Discussion on "The Metallography of Copper Containing Small Amounts of Bismuth", 660; elected student member, xx.
- Whymper, Harry William.** Elected member, xx.
- Wilkinson, R. G., and F. A. Fox.** Paper: "The Hot Working of Magnesium and Its Alloys", 473; reply to discussion, 758, 761, 763.
- Williams, Clifford Douglas.** Elected student member, xxii.
- Williams, Cyril Hector.** Elected member, xviii.
- Williams, Sidney Jonas.** Elected member, xvii.
- Wilms, G. R.** Paper: "Note on the Use of Electropolishing in the Metallographic Study of Plastic Deformation", 629.
- Wilson, Clifford.** Elected member, xvii.
- Wingrove, David John.** Elected student member, xxii.
- Wood, W. A., and W. A. Rachinger.** Paper: "The Mechanism of Deformation in Metals, with Special Reference to Creep", 237; remarks at opening of discussion, 730; reply to discussion, 736.
- von Zeerleder, A.** Discussion on "Modern Billet Casting, with Special Reference to the Solidification Process", 667.